Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Imformation

Palladium-Catalyzed *para*-Selective Arylation of Phenols with Aryl Iodides in Water

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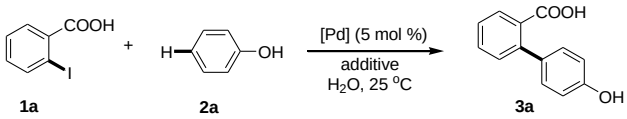
1. General methods

Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF254 plates. Column chromatography was performed using silica gel (300-400mesh) eluting with ethyl acetate, petroleum and acetic acid. All products were characterized by their NMR and HRMS. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz (Bruker DPX) with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts are reported in ppm using TMS as internal standard. HRMS was recorded on a commercial apparatus (ESI Source, TOF).

2. Table S1 Optimization of reaction conditions.[a]



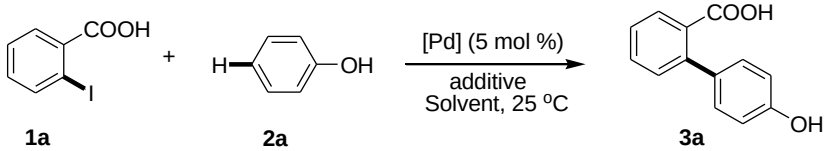
1a **2a** **3a**

Entry	[Pd]	Additive	Time [h]	Yield [%][b]
1	$Pd(OAc)_2$	AgOAc	12	trace
2	$Pd(OAc)_2$	$AgBF_4$	12	45
3	$Pd(OAc)_2$	Ag_2CO_3	12	trace
4	$Pd(OAc)_2$	$AgSbF_6$	12	54
5	$Pd(OAc)_2$	AgOTf	12	50
6	$Pd(OAc)_2$	AgTFA	12	55
7	$Pd(OAc)_2$	AgTFA	24	85
8	$PdCl_2$	AgTFA	24	65
9	$Pd[P(Ph)_3]_4$	AgTFA	24	28
10	-	AgTFA	24	-
11	$Pd(OAc)_2$	-	24	-
12	$Pd(OAc)_2$	AgTFA	24	84[c]

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (0.02 mmol), Ag salts (0.44 mmol), H_2O (0.8 mL), rt. [b] Yield of isolated product. [c] Reaction was performed at 50 °C. OTf = trifluoromethanesulfonate, TFA = trifluoroacetate.

3. Organic solvents screening

Table S2. Organic solvents screening for reaction between phenol and 2-iodobenzoic acid.[a]

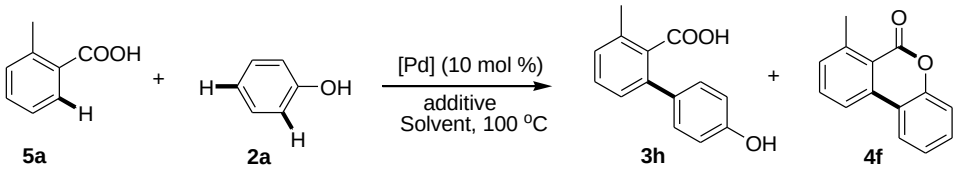


1a **2a** **3a**

Entry	[Pd]	Additive	Solvent	Time [h]	Yield [%]
1	$Pd(OAc)_2$	AgTFA	EtOH	24	trace
2	$Pd(OAc)_2$	AgTFA	MeOH	24	trace
3	$Pd(OAc)_2$	AgTFA	CH_3CN	24	trace
4	$Pd(OAc)_2$	AgTFA	NMP	24	trace
5	$Pd(OAc)_2$	AgTFA	EtOAc	24	trace
6	$Pd(OAc)_2$	AgTFA	AcOH	24	trace
7	$Pd(OAc)_2$	AgTFA	DCE	24	28
8	$Pd(OAc)_2$	AgTFA	dioxane	24	trace
9	$Pd(OAc)_2$	AgTFA	Tol	24	25
10	$Pd(OAc)_2$	AgTFA	DMSO	24	0
11	$Pd(OAc)_2$	AgTFA	DMF	24	0

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (0.02 mmol), Ag salts (0.44 mmol), Solvetnt (0.8 mL), rt.

Table S3. Organic solvents screening for oxidative C–H/C–H cross-coupling reaction. [a]



5a **2a** **3h** **4f**

Entry	[Pd]	Additive	Solvent	Time [h]	Yield [%]
1	$Pd(OAc)_2$	AgTFA	EtOH	24	0
2	$Pd(OAc)_2$	AgTFA	MeOH	24	0
3	$Pd(OAc)_2$	AgTFA	CH_3CN	24	0
4	$Pd(OAc)_2$	AgTFA	NMP	24	0
5	$Pd(OAc)_2$	AgTFA	EtOAc	24	0
6	$Pd(OAc)_2$	AgTFA	AcOH	24	0
7	$Pd(OAc)_2$	AgTFA	DCE	24	0
8	$Pd(OAc)_2$	AgTFA	dioxane	24	0
9	$Pd(OAc)_2$	AgTFA	Tol	24	0
10	$Pd(OAc)_2$	AgTFA	DMSO	24	trace
11	$Pd(OAc)_2$	AgTFA	DMF	24	trace
12	$Pd(OAc)_2$	AgTFA	t-BuOH	24	0
13	$Pd(OAc)_2$	AgTFA	Solvent-free	24	trace

[a] Reaction conditions: **5a** (0.4 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (0.04 mmol), Ag salts (0.8 mmol), Solvetnt (1 mL),100^{o}C.

4. General experimental procedures

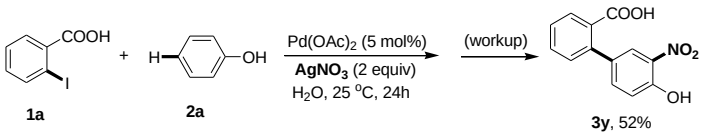
The general procedure for *para*-selective arylation of phenols:

Aryl iodides (0.4 mmol), phenols (1 mmol), $Pd(OAc)_2$ (0.02 mmol), and AgTFA (0.44 mmol) were combined in water (0.8 mL) in a 10 mL vial. The reaction mixture was stirred at the indicated temperature for 24 hours without an inert gas atmosphere. The mixture was then extracted with ethyl acetate (3x10mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (eluted with petroleum ether/ethyl acetate/ acetic acid 100:40:1) to afford the corresponding products.

The general procedure for the synthesis of dibenzopyranones:

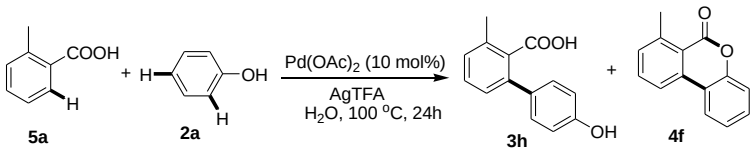
Aryl iodides (0.4 mmol), *para*-substituted phenols (1 mmol), $Pd(OAc)_2$ (0.02 mmol), AgTFA (0.44 mmol), and TsOH (0.1 mmol) were combined in water (0.8 mL) in a 10 mL vial. The reaction mixture was stirred at 25 ^{o}C for 24 hours without an inert gas atmosphere. The mixture was then extracted with ethyl acetate (3x10mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (eluted with petroleum ether/ethyl acetate/ acetic acid 100:5:1) to afford the corresponding products.

The procedure for tandem C–H arylation/nitration:



o-iodobenzoic acid (0.4 mmol), phenol (1 mmol), $Pd(OAc)_2$ (0.02 mmol), and $AgNO_3$ (0.8 mmol) were combined in water (0.8 mL) in a 10 mL vial. The reaction mixture was stirred at 25 ^{o}C for 24 hours without an inert gas atmosphere. The mixture was then extracted with ethyl acetate (3x10mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure (50 ^{o}C for 10 min). The residue was purified by silica-gel column chromatography (eluted with petroleum ether/ethyl acetate/ acetic acid 100:40:1) to afford the corresponding product.

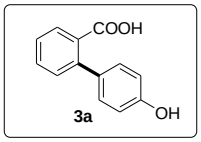
The procedure for C–H/ C–H oxidative coupling:



o-toluic acid (0.4 mmol), phenol (2 mmol), $Pd(OAc)_2$ (0.04 mmol), and AgTFA (0.8 mmol) were combined in water (1 mL) in a 10 mL vial. The reaction mixture was stirred at 100 ^{o}C for 24 hours without an inert gas atmosphere. After cooled to room temperature, the mixture was then extracted with ethyl acetate (3x10mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (eluted with petroleum ether/ethyl acetate/ acetic acid 100:5:1 to 100:40:1) to afford the corresponding products.

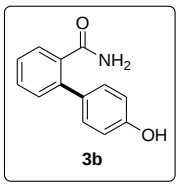
5. Characterization data for products

2-(4-Hydroxyphenyl)benzoic acid (3a)[1]



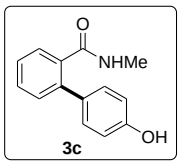
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.79 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 9.51 (s, 1H), 12.71 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 114.97, 126.44, 128.76, 129.36, 130.14, 130.55, 131.29, 132.33, 140.62, 156.80, 170.11.
ESI-MS: calculated $[C_{13}H_9O_3]^-$: 213.0552, found: 213.0552.

2-(4-Hydroxyphenyl)benzamide (3b)



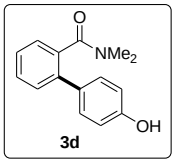
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.77 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.27 (s, 1H), 7.30-7.44 (m, 4H), 7.54 (s, 1H), 9.48 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 115.03, 126.23, 127.49, 129.08, 129.50, 129.64, 131.06, 137.14, 138.77, 156.82, 171.51.
ESI-MS: calculated $[C_{13}H_{11}NO_2Na]^+$: 236.0687, found: 236.0686.

2-(4-Hydroxyphenyl)-*N*-methylbenzamide (3c)



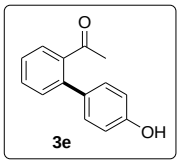
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.57 (d, J = 4.4 Hz, 3H), 6.77 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.32-7.34 (m, 3H), 7.41-7.44 (m, 1H), 7.95 (d, J = 4.8 Hz, 1H), 9.50 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 25.96, 115.08, 126.28, 127.61, 129.17, 129.37, 129.53, 130.85, 137.07, 138.83, 156.81, 170.04.
ESI-MS: calculated $[C_{14}H_{13}NO_2Na]^+$: 250.0844, found: 250.0848.

2-(4-Hydroxyphenyl)-*N*,*N*-dimethylbenzamide (3d)



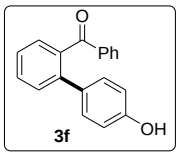
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.39 (s, 3H), 2.77 (s, 3H), 6.80 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.6 Hz, 1H), 7.34-7.38 (m, 2H), 7.43-7.47 (m, 1H), 9.58 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 33.98, 37.44, 115.30, 126.79, 127.11, 128.94, 129.12, 129.25, 130.30, 135.55, 138.02, 157.07, 170.25.
ESI-MS: calculated $[C_{15}H_{15}NO_2Na]^+$: 264.1000, found: 264.0995.

4-(2-Acetylphenyl)phenol (3e)



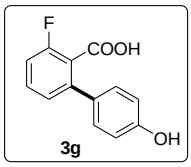
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.07 (s, 3H), 6.71 (s, 1H), 6.89 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.37-7.40 (m, 2H), 7.48-7.54 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): 30.49, 115.80, 127.07, 127.79, 130.16, 130.25, 130.99, 132.72, 140.41, 140.62, 156.20, 207.06.
ESI-MS: calculated $[C_{14}H_{11}O_2]^-$: 211.0759, found: 211.0765.

Methanone, (4'-hydroxy[1,1'-biphenyl]-2-yl)phenyl- (3f)



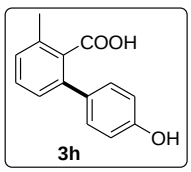
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.62 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.42-7.63 (m, 7H), 9.48 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 115.25, 126.60, 128.26, 128.45, 129.36, 129.67, 129.86, 130.45, 133.14, 136.78, 138.28, 140.12, 156.84, 198.18.
ESI-MS: calculated $[C_{19}H_{13}O_2]^-$: 273.0916, found: 273.0921.

6-Fluoro-2-(4-hydroxyphenyl)benzoic acid (3g)



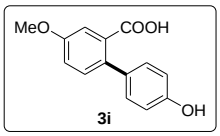
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.83 (d, J = 8.4 Hz, 2H), 7.21-7.27 (m, 4H), 7.47-7.52 (m, 1H), 9.69 (s, 1H), 13.34 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 113.58 (d, J_{CF} = 21.4 Hz), 115.36, 122.54 (d, J_{CF} = 18.2 Hz), 125.36 (d, J_{CF} = 2.4 Hz), 129.29, 129.37(d, J_{CF} = 2.4 Hz), 130.78 (d, J_{CF} = 9 Hz), 140.69 (d, J_{CF} = 3.6 Hz), 157.43, 158.42 (d, J_{CF} = 244.1 Hz), 166.74.
ESI-MS: calculated $[C_{13}H_8FO_3]^-$: 231.0457, found: 231.0455.

6-Methyl-2-(4-hydroxyphenyl)benzoic acid (3h)



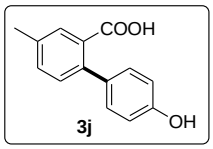
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.31 (s, 3H), 6.79 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 7.6 Hz, 1H), 7.20-7.22 (m, 3H), 7.33 (t, J = 7.6 Hz, 1H), 9.56 (s, 1H), 12.95 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 19.25, 115.11, 126.85, 128.13, 128.61, 129.28, 131.06, 133.58, 134.70, 138.20, 156.88, 170.82.
ESI-MS: calculated $[C_{14}H_{11}O_3]^-$: 227.0708, found: 227.0711.

5-Methoxy-2-(4-hydroxyphenyl)benzoic acid (3i)



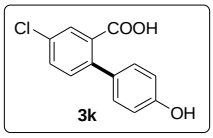
^{1}H NMR (400 MHz, DMSO-d_6): δ 3.81 (s, 3H), 6.77 (d, J = 8.8 Hz, 2H), 7.07-7.12 (m, 3H), 7.16 (d, J = 7 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 9.46 (s, 1H), 12.74 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 55.32, 113.66, 114.90, 116.32, 129.31, 131.07, 131.42, 133.07, 133.29, 156.43, 157.60, 169.82.
ESI-MS: calculated $[C_{14}H_{11}O_4]^-$: 243.0657, found: 243.0660.

5-Methyl-2-(4-hydroxyphenyl)benzoic acid (3j)



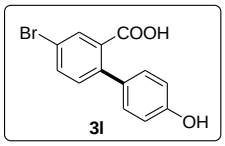
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.35 (s, 3H), 6.77 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 9.47 (s, 1H), 12.60 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 20.34, 114.92, 129.17, 129.30, 130.07, 131.13, 131.25, 132.12, 135.76, 137.84, 156.61, 170.18.
ESI-MS: calculated $[C_{14}H_{11}O_3]^-$: 227.0708, found: 227.0710.

5-Chloro-2-(4-hydroxyphenyl)benzoic acid (3k)



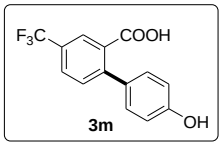
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.80 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.56-7.66 (m, 2H), 9.67 (s, 1H), 12.99 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 115.09, 128.23, 129.39, 129.97, 130.27, 131.11, 132.02, 134.15, 139.33, 157.10, 168.76.
ESI-MS: calculated $[C_{13}H_8ClO_3]^-$: 247.0162, 249.0132, found: 247.0162, 249.0149.

5-Bromo-2-(4-hydroxyphenyl)benzoic acid (3l)



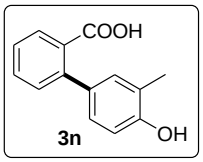
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.85 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.74-7.84 (m, 2H), 9.65 (s, 1H), 13.08 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 115.10, 119.39, 129.34, 129.99, 131.08, 132.28, 133.23, 134.35, 139.70, 157.13, 168.63.
ESI-MS: calculated $[C_{13}H_8BrO_3]^-$: 290.9657, 292.9636, found: 290.9659, 292.9652.

5-Trifluoromethyl-2-(4-hydroxyphenyl)benzoic acid (3m)



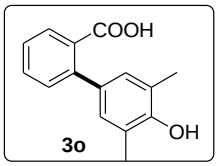
^{1}H NMR (400 MHz, DMSO-d_6): δ 6.86 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H), 9.71 (s, 1H), 13.18 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 115.21, 123.90 (q, J_{CF} = 270 Hz), 125.45 (q, J_{CF} = 4 Hz), 127.03 (q, J_{CF} = 32 Hz), 127.04 (q, J_{CF} = 4 Hz), 129.53, 129.75, 131.26, 133.11, 144.55, 157.57, 168.86.
ESI-MS: calculated $[C_{14}H_8F_3O_3]^-$: 281.0426, found: 281.0429.

2-(3-Methyl-4-hydroxyphenyl)benzoic acid (3n)



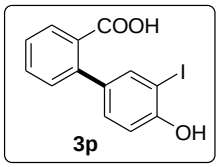
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.15 (s, 3H), 6.81 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 7.06 (s, 1H), 7.32-7.38 (m, 2H), 7.47-7.51 (m, 1H), 7.63 (d, J = 6.8 Hz, 1H), 9.43 (s, 1H), 12.65 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 16.06, 114.32, 123.46, 126.31, 126.63, 128.65, 130.11, 130.44, 130.52, 131.25, 132.43, 140.73, 154.92, 170.27.
ESI-MS: calculated $[C_{14}H_{11}O_3]^-$: 227.0708, found: 227.0711.

2-(3,5-Dimethyl-4-hydroxyphenyl)benzoic acid (3o)



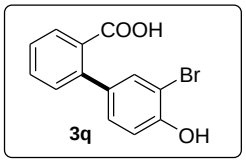
^{1}H NMR (400 MHz, DMSO-d_6): δ 2.18 (s, 6H), 6.89 (s, 2H), 7.32-7.38 (m, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 8.33 (s, 1H), 12.68 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 16.69, 123.83, 126.30, 128.13, 128.57, 130.10, 130.39, 131.56, 132.43, 140.73, 152.71, 170.28.
ESI-MS: calculated $[C_{15}H_{13}O_3]^-$: 241.0865, found: 241.0867.

2-(3-Iodo-4-hydroxyphenyl)benzoic acid (3p)



^{1}H NMR (400 MHz, DMSO-d_6): δ 6.92 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.60 (s, 1H), 7.68 (d, J = 7.6 Hz, 1H), 10.46 (s, 1H), 12.83 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 84.21, 114.54, 126.98, 128.98, 129.59, 130.26, 130.79, 132.09, 133.52, 138.15, 139.23, 156.02, 169.72.
ESI-MS: calculated $[C_{13}H_8IO_3]^-$: 338.9518, found: 338.9508.

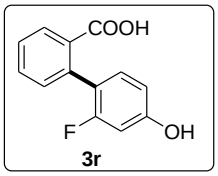
2-(3-Bromo-4-hydroxyphenyl)benzoic acid (3q)



^{1}H NMR (400 MHz, DMSO-d_6): δ 6.98 (d, J = 8.4 Hz, 1H), 7.14-7.17 (m, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.41-7.44 (m, 2H), 7.52-7.56 (m, 1H), 7.69 (d, J = 7.6 Hz, 1H), 10.39 (s, 1H), 12.83 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 108.85, 115.96, 127.06, 128.76, 129.02, 130.30, 130.83, 132.08, 132.27, 133.06, 139.33, 153.41, 169.67.

ESI-MS: calculated $[C_{13}H_8BrO_3]^-$: 290.9657, 192.9636, found: 290.9646, 292.9609.

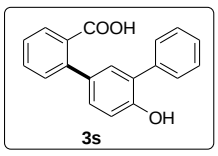
2-(2-Fluoro-4-hydroxyphenyl)benzoic acid (3r)



^{1}H NMR (400 MHz, DMSO-d_6): δ 6.54-6.58 (m, 1H), 6.64-6.67 (m, 1H), 7.13(t, J = 8.8 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 10.08 (s, 1H), 12.37 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 102.2 (d, J_{CF} = 25 Hz), 111.36, 119.4 (d, J_{CF} = 16 Hz), 127.35, 129.44, 130.98 (d, J_{CF} = 6 Hz), 131.21, 131.30, 135.49, 158.43 (d, J_{CF} = 12 Hz), 159.49 (d, J_{CF} = 242 Hz), 168.93.

ESI-MS: calculated $[C_{13}H_8FO_3]^-$: 231.0457, found: 231.0456.

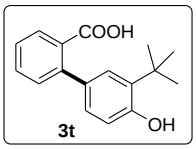
2-(3-Phenyl-4-hydroxyphenyl)benzoic acid (3s)



^{1}H NMR (400 MHz, DMSO-d_6): δ 7.00 (d, J = 8.4 Hz, 1H), 7.18-7.24 (m, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.38-7.45 (m, 4H), 7.53 (t, J = 7.6 Hz, 1H), 7.59 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 7.6 Hz, 1H), 9.73 (s, 1H), 12.81 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 115.21, 118.36, 126.38, 126.57, 127.79, 128.01, 129.01, 129.40, 130.11, 130.75, 131.15, 131.26, 136.84, 140.90, 141.82, 154.29, 169.07.

ESI-MS: calculated $[C_{19}H_{13}O_3]^-$: 289.0865, found: 289.0862.

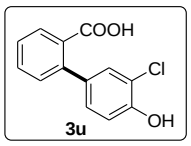
2-(3-*t*-Butyl-4-hydroxyphenyl)benzoic acid (3t)



^{1}H NMR (400 MHz, DMSO-d_6): δ 1.40 (s, 9H), 6.86 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.19 (s, 1H), 7.35-7.40 (m, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 9.51 (s, 1H), 12.52 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 29.26, 34.27, 116.01, 126.18, 126.43, 126.83,

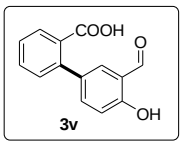
128.54, 129.94, 130.37, 130.65, 132.62, 134.67, 140.81, 155.44, 170.58.
ESI-MS: calculated $[C_{17}H_{17}O_3]^-$: 269.1178, found: 269.1180.

2-(3-Chloro-4-hydroxyphenyl)benzoic acid (3u)



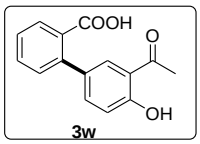
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.05 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 10.35 (s, 1H), 12.88 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 116.29, 119.22, 127.06, 128.08, 129.02, 129.38, 130.28, 130.82, 132.11, 132.67, 139.44, 152.40, 169.67.
ESI-MS: calculated $[C_{13}H_8ClO_3]^-$: 247.0162, 249.0132, found: 247.0162, 249.0154.

2-(3-Formyl-4-hydroxyphenyl)benzoic acid (3v)



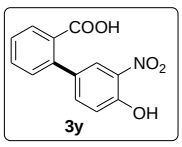
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.04 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.43-7.51 (m, 2H), 7.55-7.60 (m, 2H), 7.74 (d, J = 7.6 Hz, 1H), 10.31 (s, 1H), 10.84 (s, 1H), 12.82 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 117.14, 121.95, 127.29, 128.31, 129.37, 130.36, 131.11, 131.89, 132.11, 136.49, 139.91, 160.15, 169.52, 191.22.
ESI-MS: calculated $[C_{14}H_9O_4]^-$: 241.0501, found: 241.0506.

2-(3-Acetyl-4-hydroxyphenyl)benzoic acid (3w)



^{1}H NMR (400 MHz, DMSO-d_6): δ 2.72 (s, 3H), 7.06 (d, J = 8.4 Hz, 1H), 7.49-7.55 (m, 3H), 7.64 (t, J = 7.6 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 12.00 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 27.81, 117.27, 120.12, 127.23, 129.28, 130.51, 130.65, 131.02, 131.74, 131.91, 136.34, 139.80, 159.98, 169.52, 204.14.
ESI-MS: calculated $[C_{15}H_{11}O_4]^-$: 255.0657, found: 255.0661.

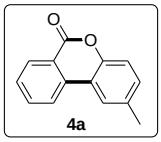
2-(3-Nitro-4-hydroxyphenyl)benzoic acid (3x)



^{1}H NMR (400 MHz, DMSO-d_6): δ 7.17 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.47-7.52 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.78-7.81 (m, 2H), 11.14 (s, 1H), 12.91 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): 118.75, 124.39, 127.67, 129.54, 130.51, 131.26, 131.64, 131.93, 135.30, 136.40,

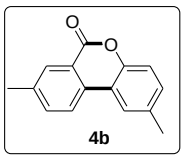
138.93, 151.32, 169.11.
ESI-MS: calculated $[C_{13}H_8NO_5]^-$: 258.0402, found: 258.0400.

2-Methylbenzo[c]chromen-6-one (4a)[2]



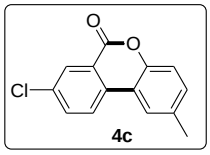
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.26-7.31 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.29, 117.66, 117.78, 121.43, 121.76, 122.90, 128.87, 130.75, 131.51, 134.25, 134.89, 134.99, 149.52, 161.56.
MS (EI, M/Z): 210 [M^+].

2,8-Dimethylbenzo[c]chromen-6-one (4b)[3]



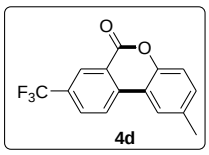
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 2.48 (s, 3H), 7.22 (s, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.24, 21.39, 117.45, 117.85, 121.16, 121.69, 122.62, 130.44, 130.90, 132.35, 134.10, 136.04, 139.11, 149.16, 161.68.
MS (EI, M/Z): 224 [M^+].

2-Methyl-8-chlorobenzo[c]chromen-6-one (4c)



^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.62-7.65 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.07, 115.73, 116.47, 121.43, 121.63, 122.25, 128.92, 130.67, 132.16, 133.42, 133.70, 133.93, 148.08, 159.12.
ESI-MS: calculated $[C_{14}H_{10}ClO_2]^+$: 245.0369, 247.0340, found: 245.0366, 247.0357.

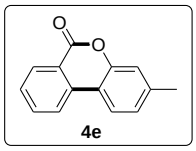
2-Methyl-8-trifluoromethylbenzo[c]chromen-6-one (4d)[4]



^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.79 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.08, 115.44, 116.73, 120.49, 121.56, 122.18, 127.01, 129.94, 131.75, 133.68, 136.64,

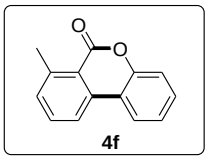
148.77, 159.24.
MS (EI, M/Z): 278 [M^+].

3-Methylbenzo[c]chromen-6-one (4e)



^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.18 (s, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.60, 115.58, 118.05, 121.03, 121.59, 122.66, 125.83, 128.53, 130.70, 134.94, 135.15, 141.45, 151.42, 161.62.
ESI-MS: calculated $[C_{14}H_{11}O_2]^+$: 211.0759, found: 211.0756.

7-Methylbenzo[c]chromen-6-one (4f)[4]



^{1}H NMR (400 MHz, $CDCl_3$): δ 2.87 (s, 3H), 7.29-7.34 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 24.06, 117.45, 118.43, 119.90, 123.17, 124.36, 130.39, 132.34, 134.09, 136.24, 144.56, 151.43, 160.61.
MS (EI, M/Z): 210 [M^+].

References:

[1] S. A. Glover, S. L. Golding, A. Goosen, C. W. Cedric, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 842.
[2] J. Luo, Y. Lu, S. Liu, J. Liu, G.-J. Deng, *Adv. Synth. Catal*. **2011**, *353*, 2604.
[3] Y. He, X. Zhang, L. Cui, J. Wang, X. Fan, *Green Chem.* **2012**, *14*, 3429.
[4] K. Vishnumurthy, A. Makriyannis, *J. Comb. Chem.* **2010**, *12*, 664.

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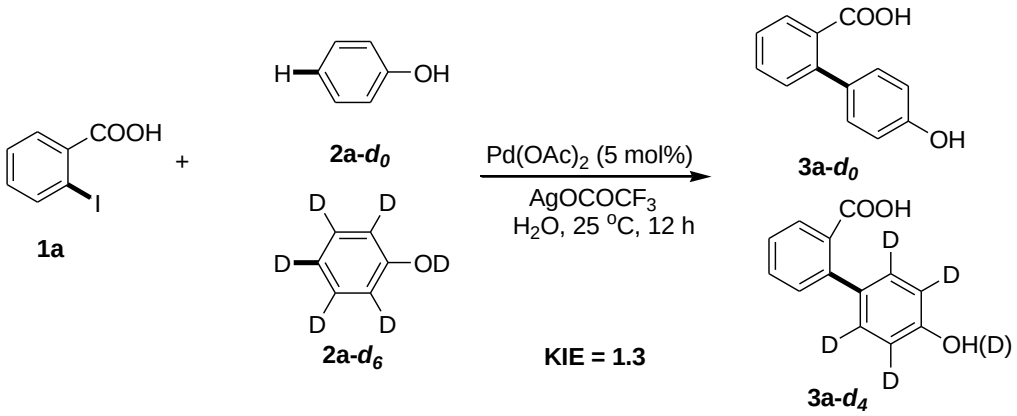
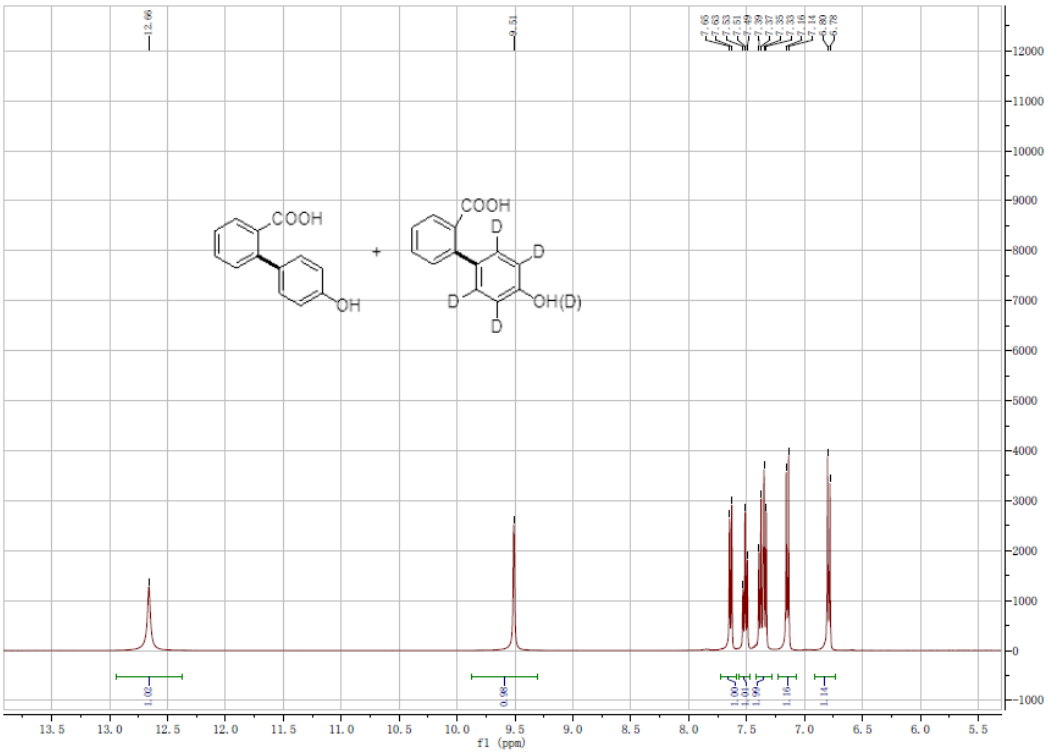
6. Kinetic isotope effect measurements:



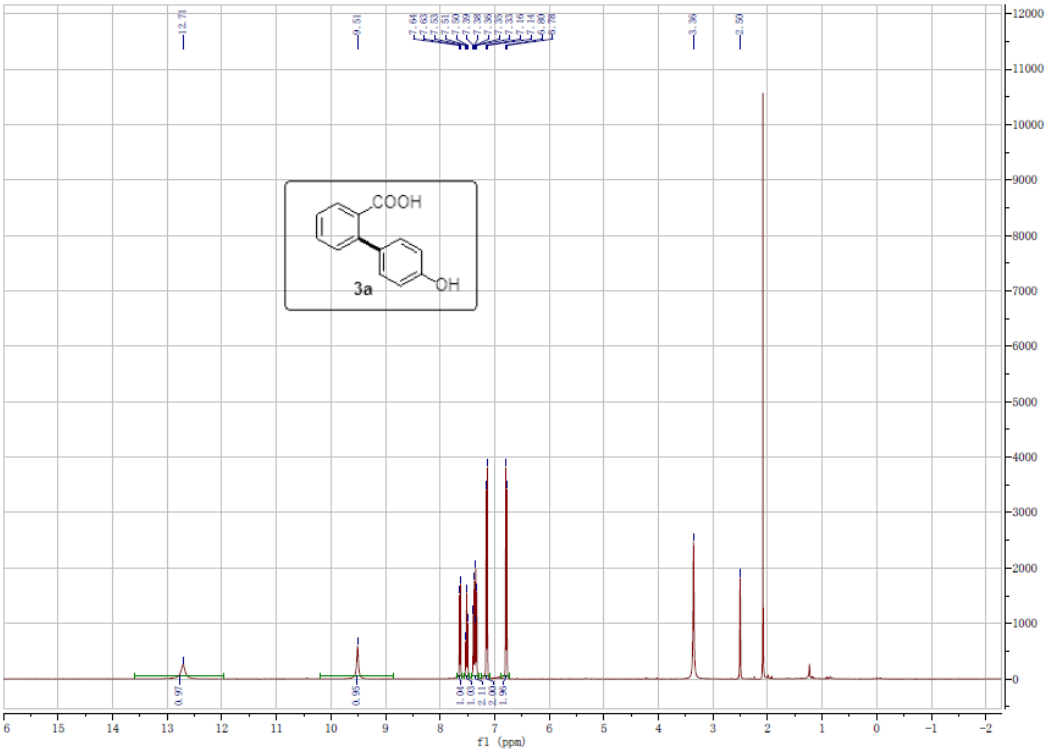
Experimental Procedure:

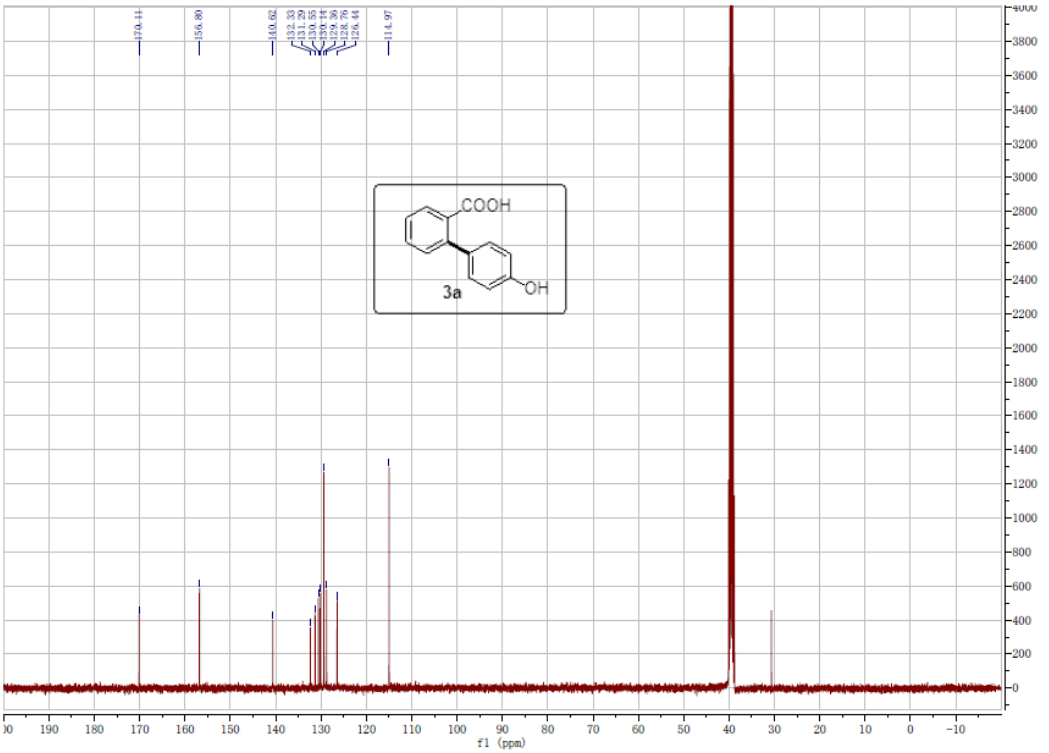
2-Iodobenzoic acid (0.4 mmol), phenol-d_0 (1 mmol), phenol-d_6 (1 mmol), $Pd(OAc)_2$ (0.02 mmol), and AgTFA (0.44 mmol) were combined in water (1 mL) in a 10 mL vial. The reaction mixture was stirred at 25 °C for 12 hours without an inert gas atmosphere. The mixture was then extracted with ethyl acetate (3x10mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography to afford the corresponding product.



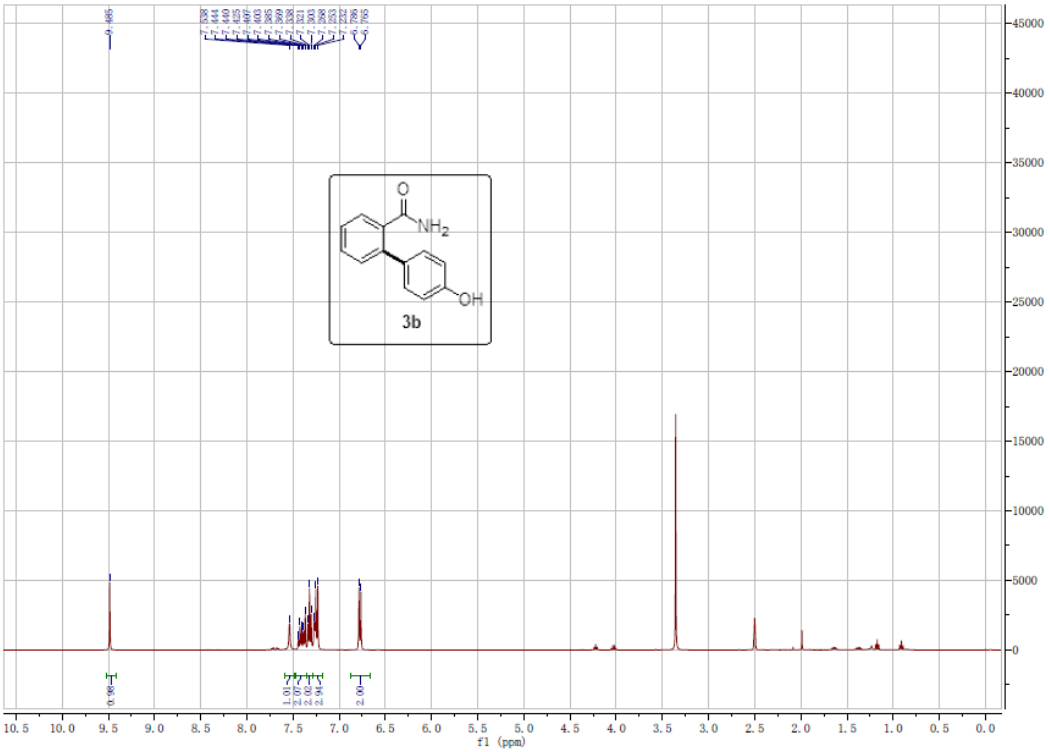
1. NMR spectra of products

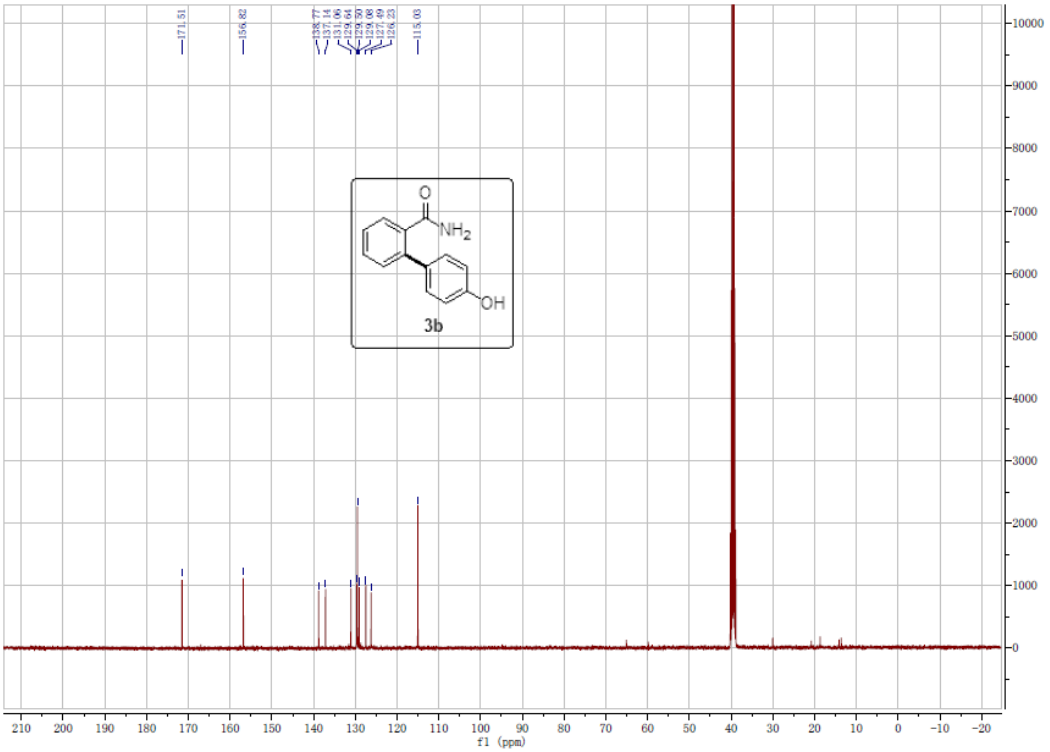
2-(4-Hydroxyphenyl)benzoic acid (3a)



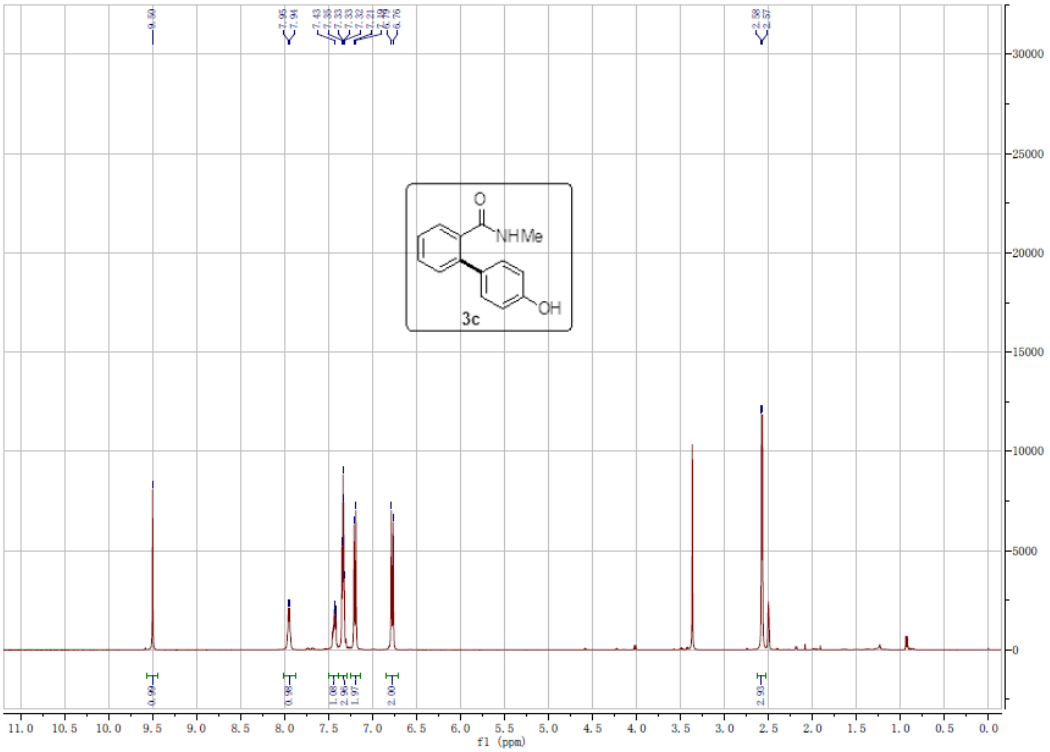


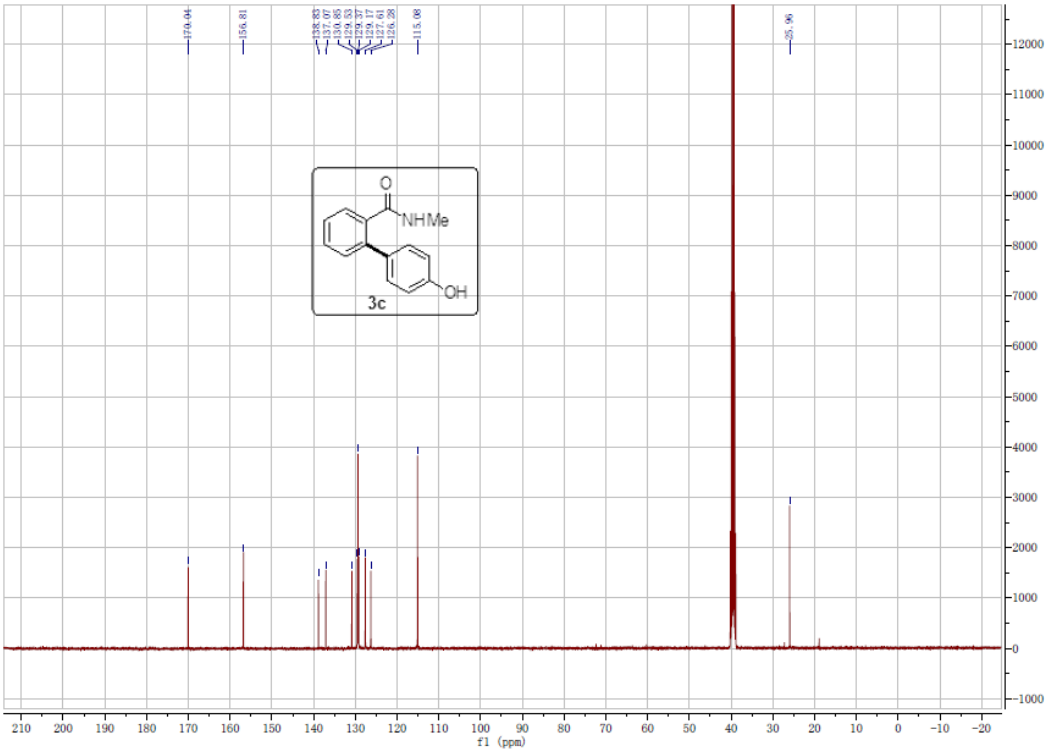
2-(4-Hydroxyphenyl)benzamide (3b)



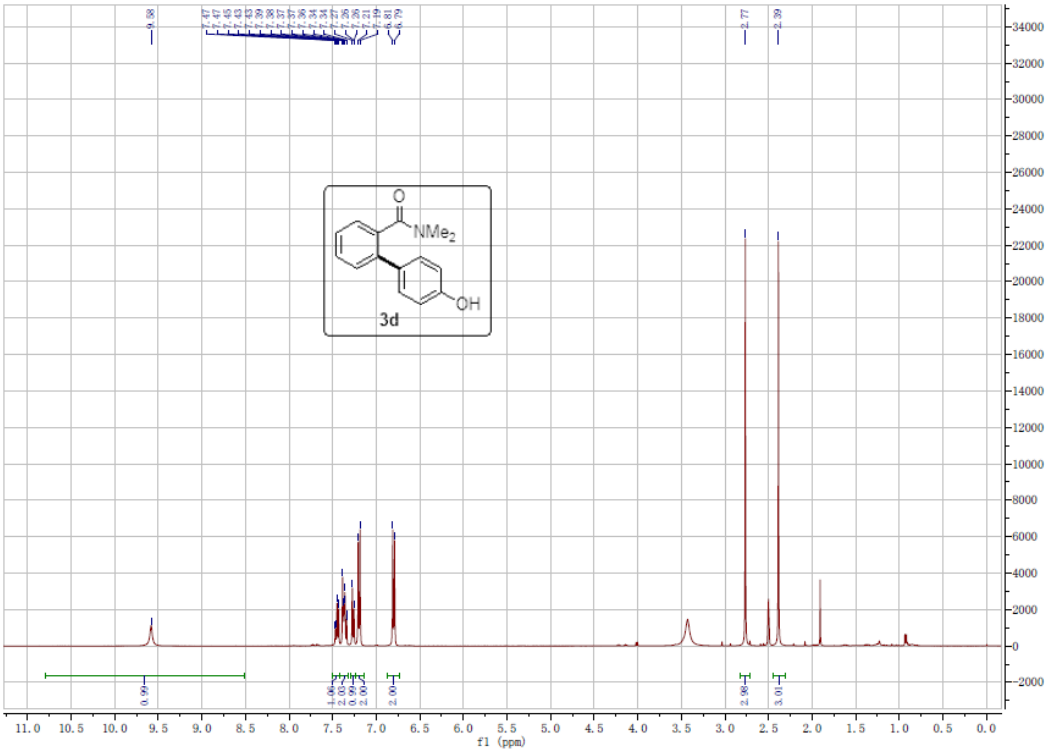


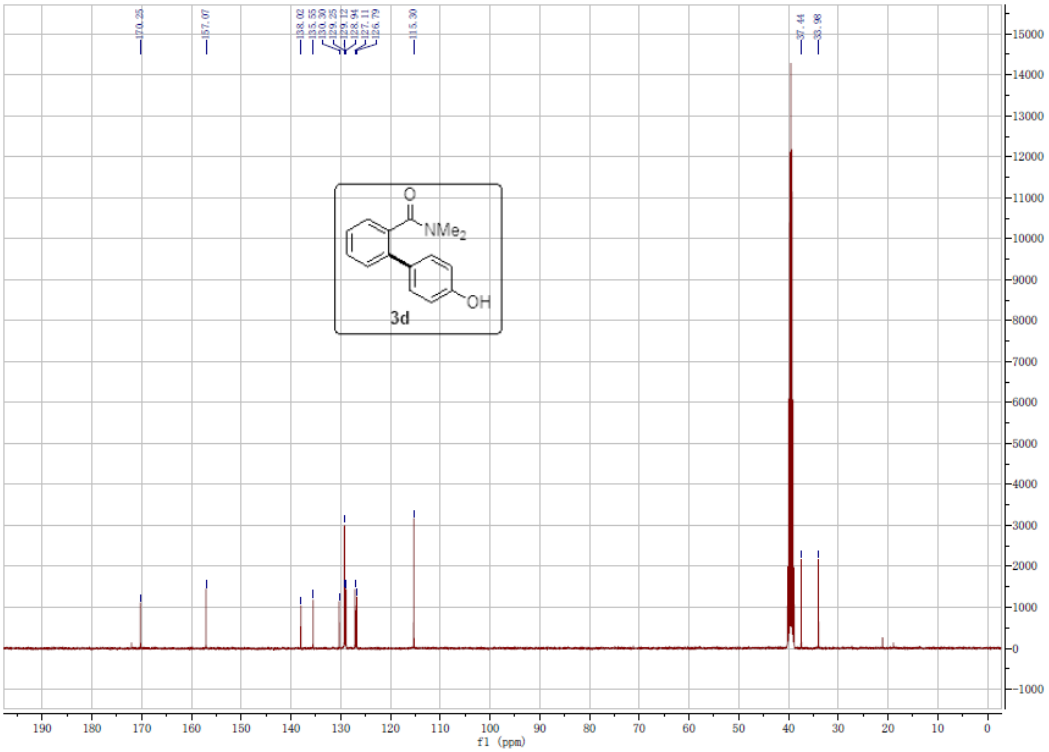
2-(4-Hydroxyphenyl)-*N*-methylbenzamide (3c)



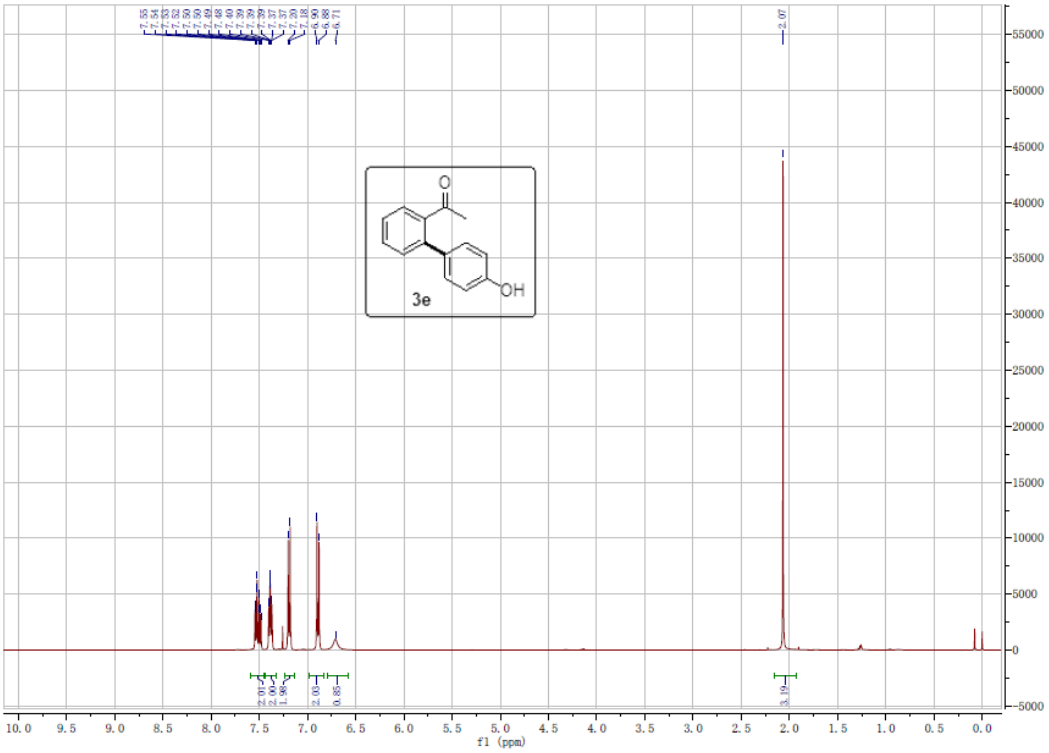


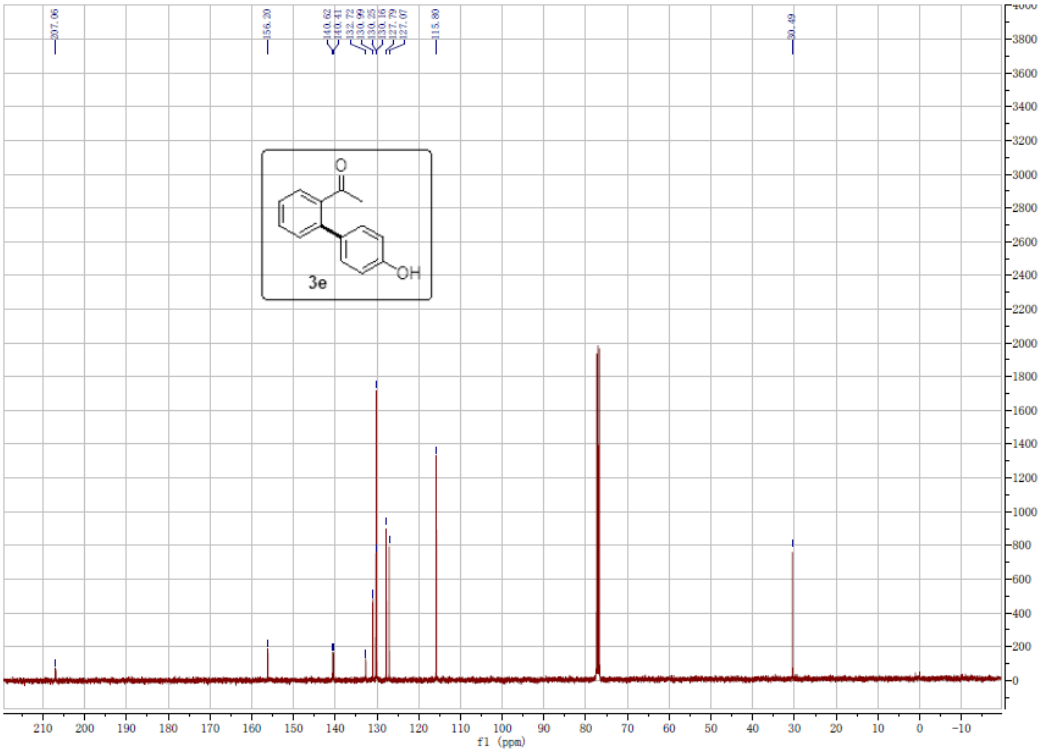
2-(4-Hydroxyphenyl)-*N*,*N*-dimethylbenzamide (3d)



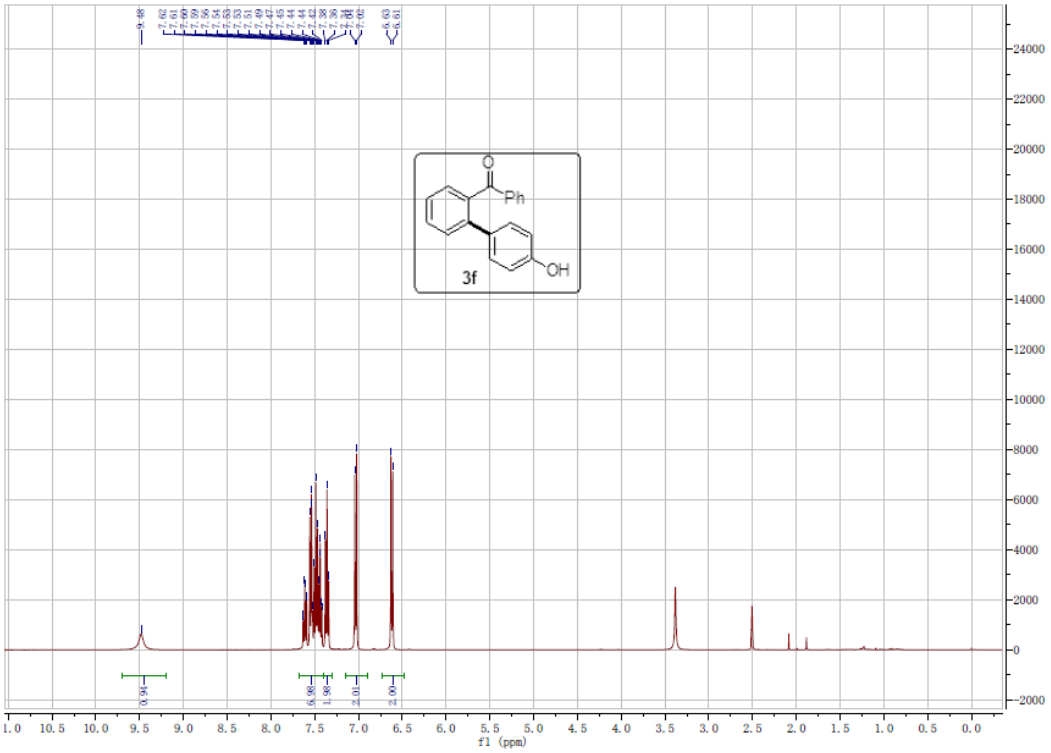


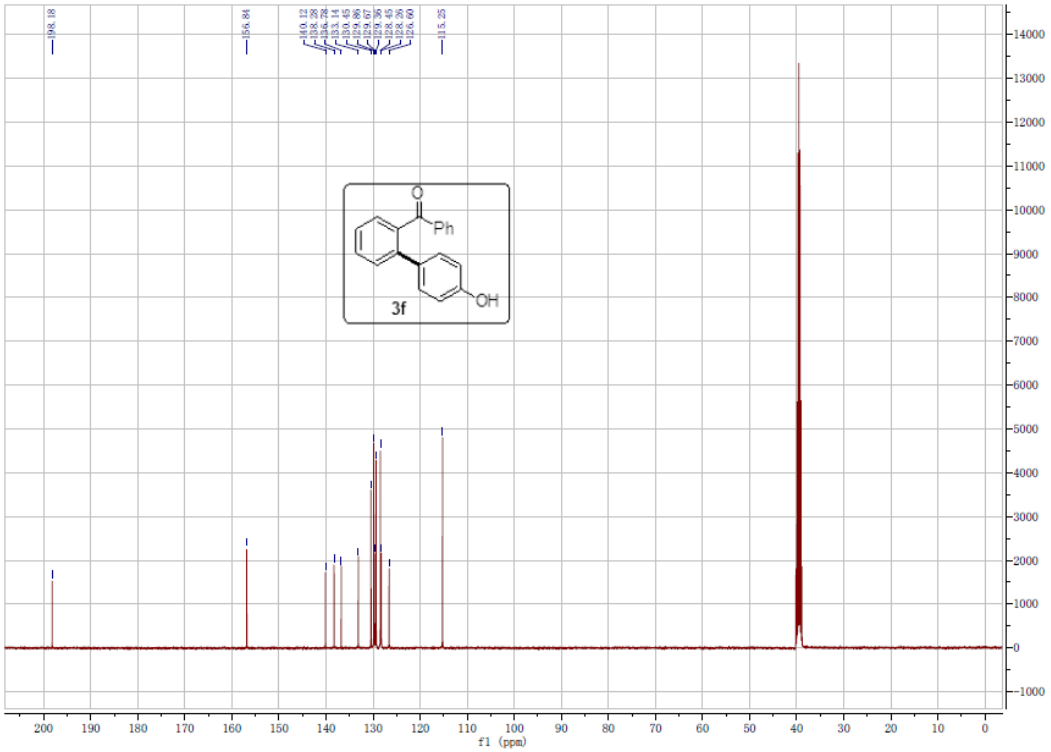
4-(2-Acetylphenyl)phenol (3e)



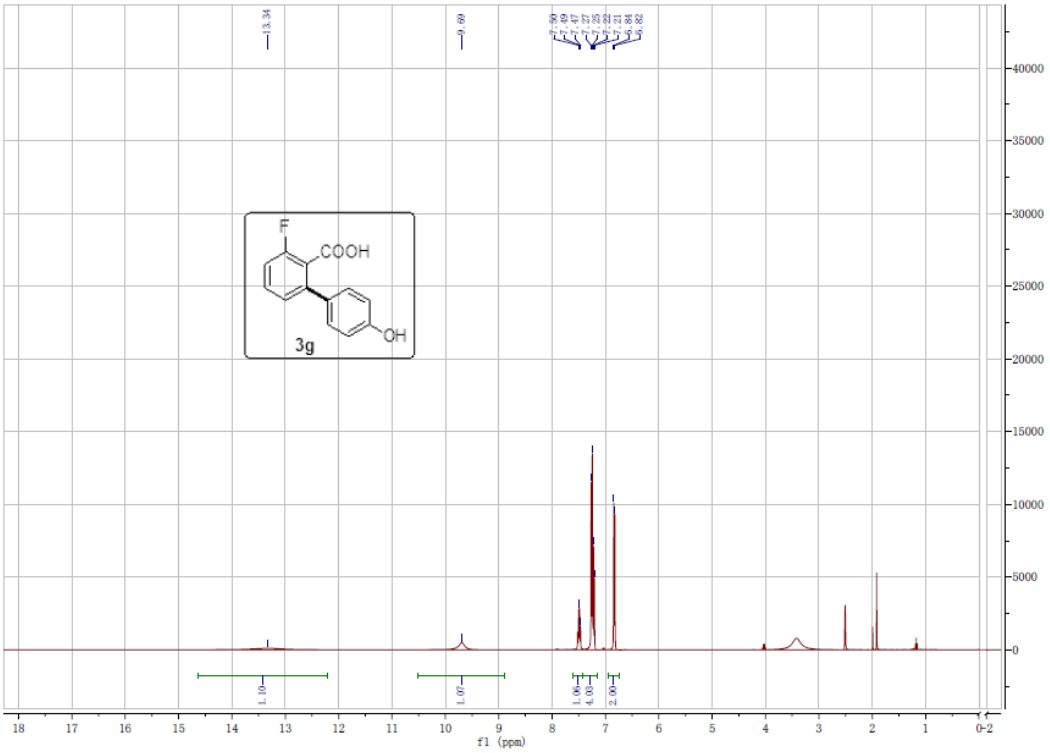


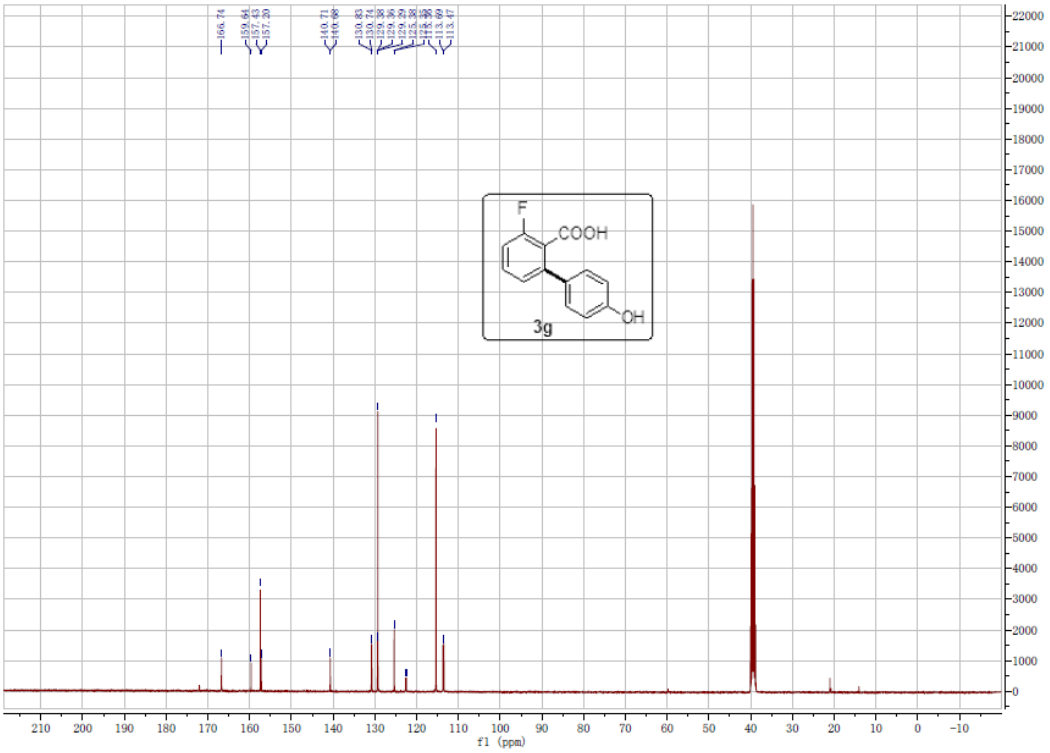
Methanone, (4'-hydroxy[1,1'-biphenyl]-2-yl)phenyl- (3f)



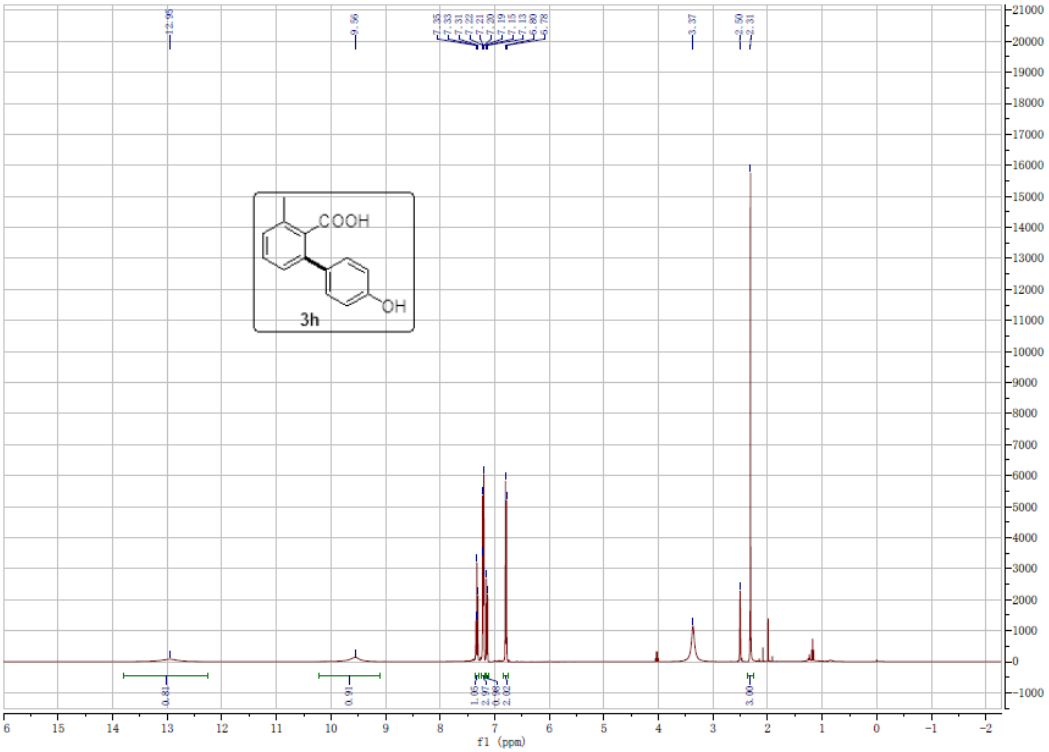


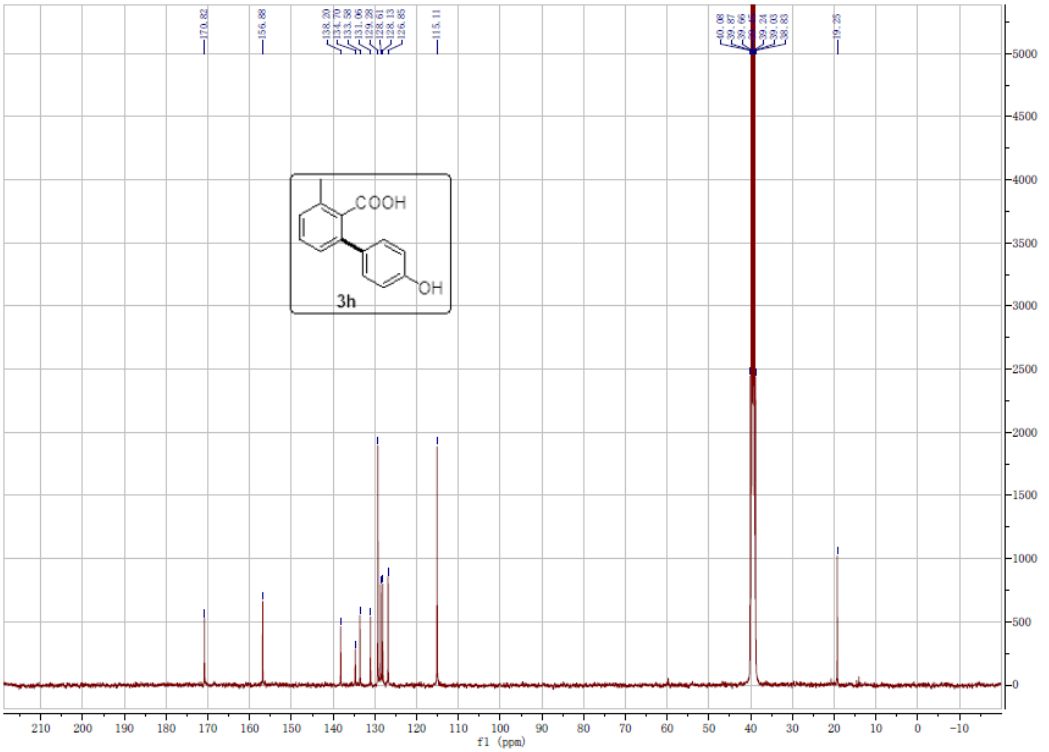
6-Fluoro-2-(4-hydroxyphenyl)benzoic acid (3g)



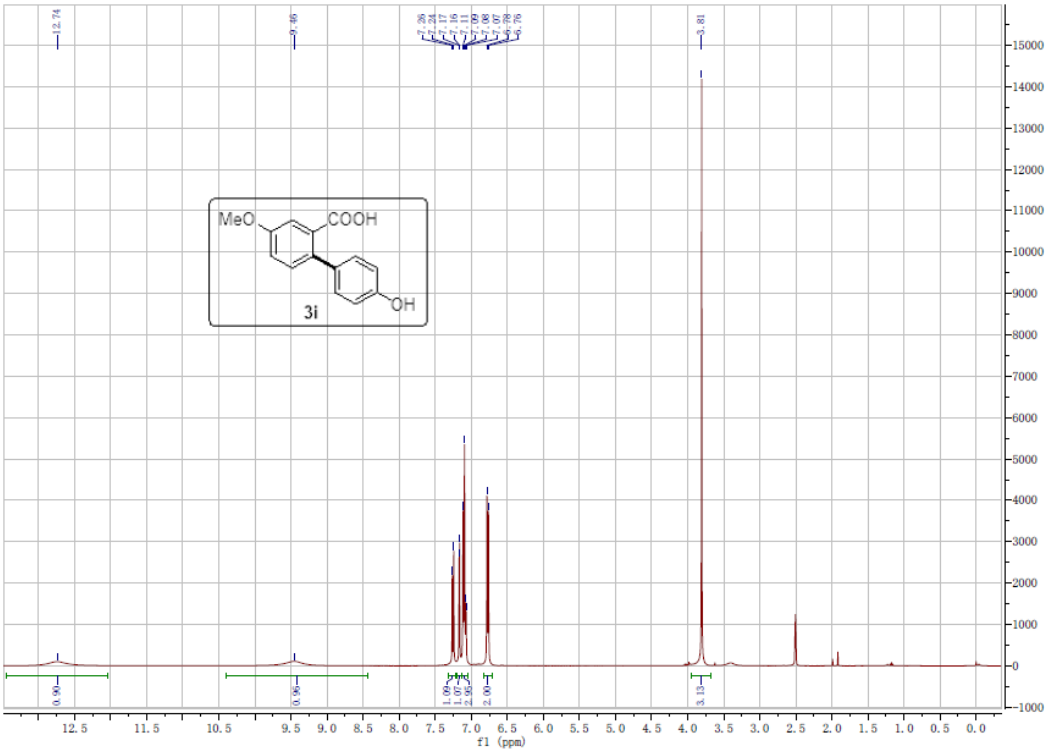


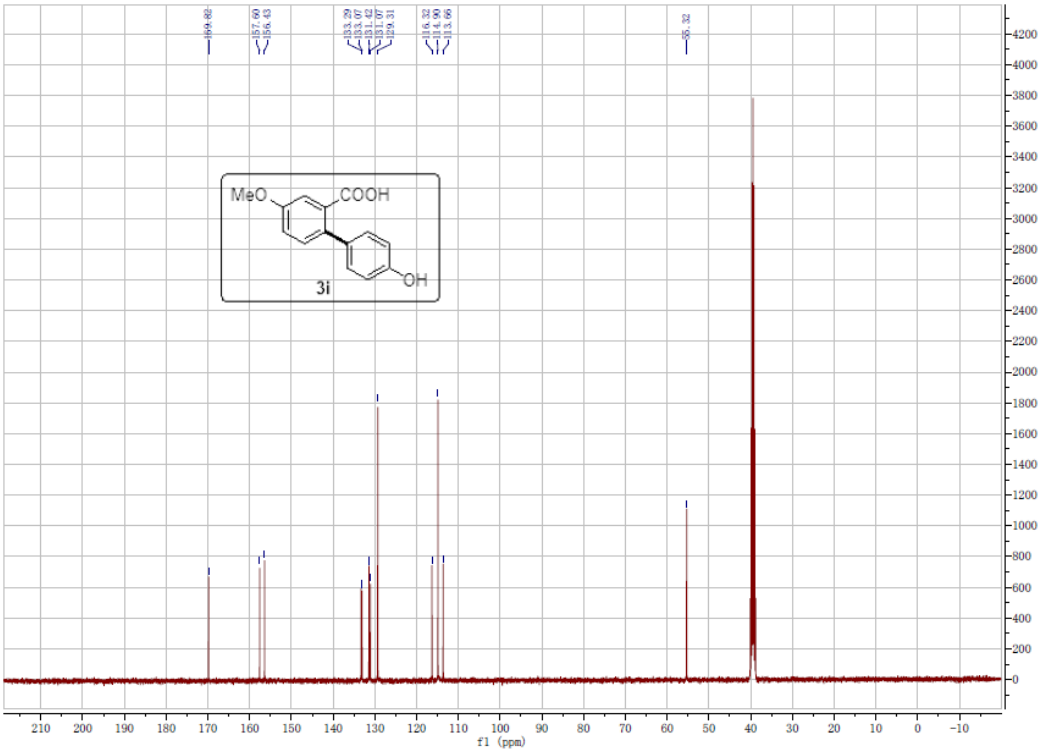
6-Methyl-2-(4-hydroxyphenyl)benzoic acid (3h)



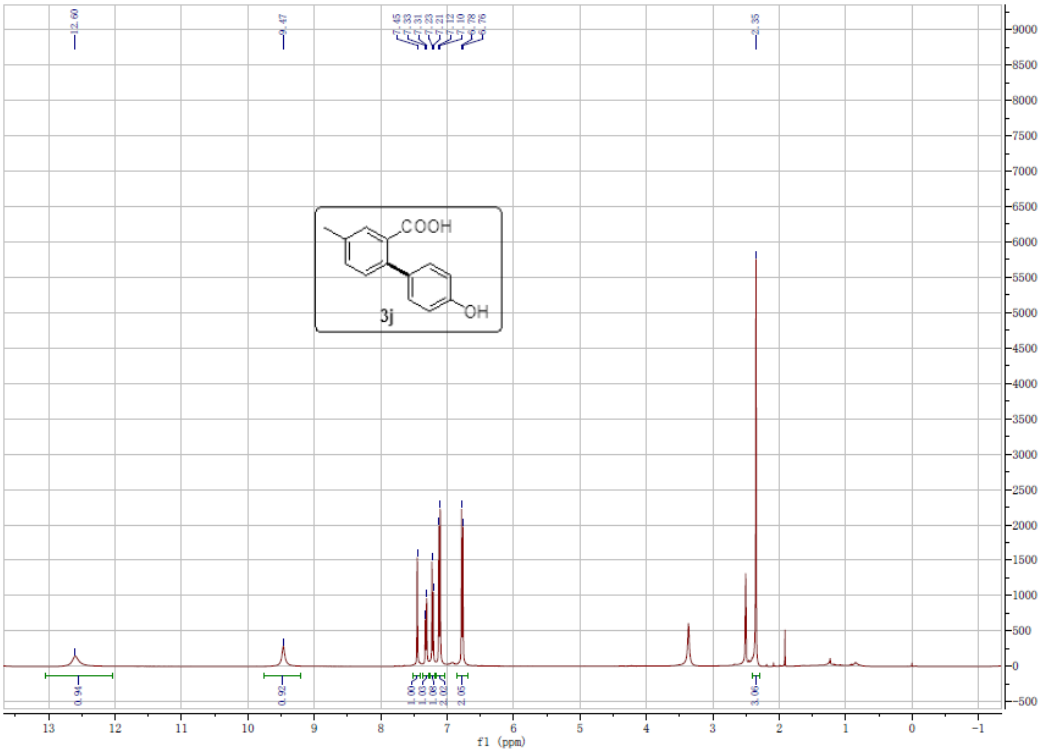


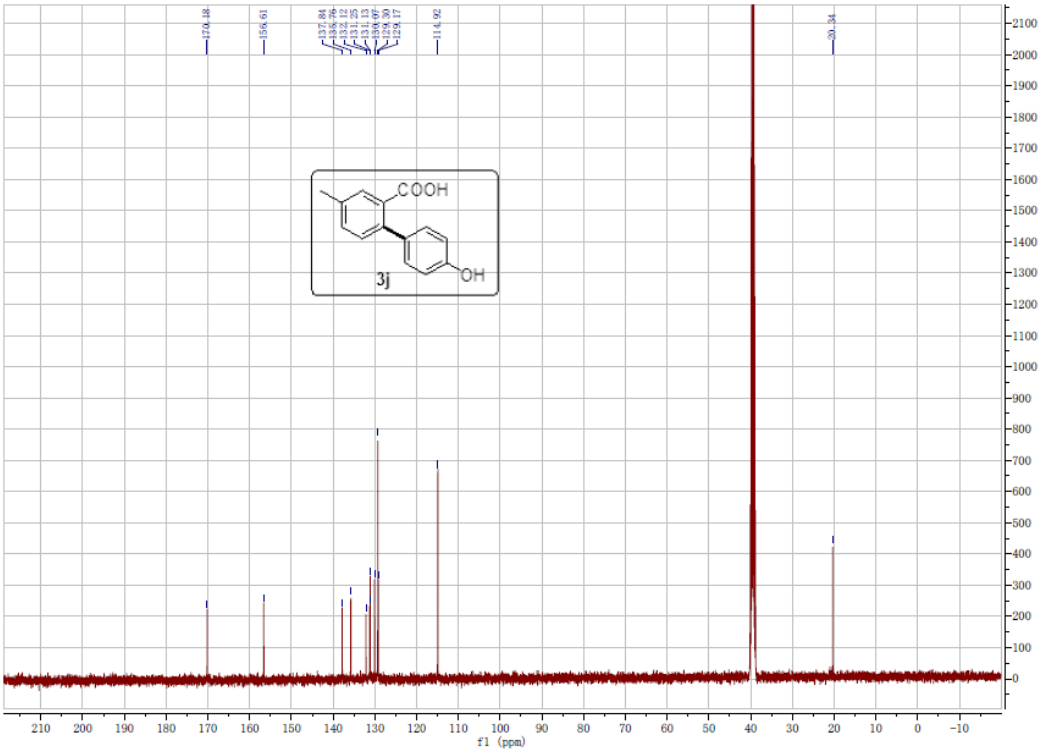
5-Methoxy-2-(4-hydroxyphenyl)benzoic acid (3i)



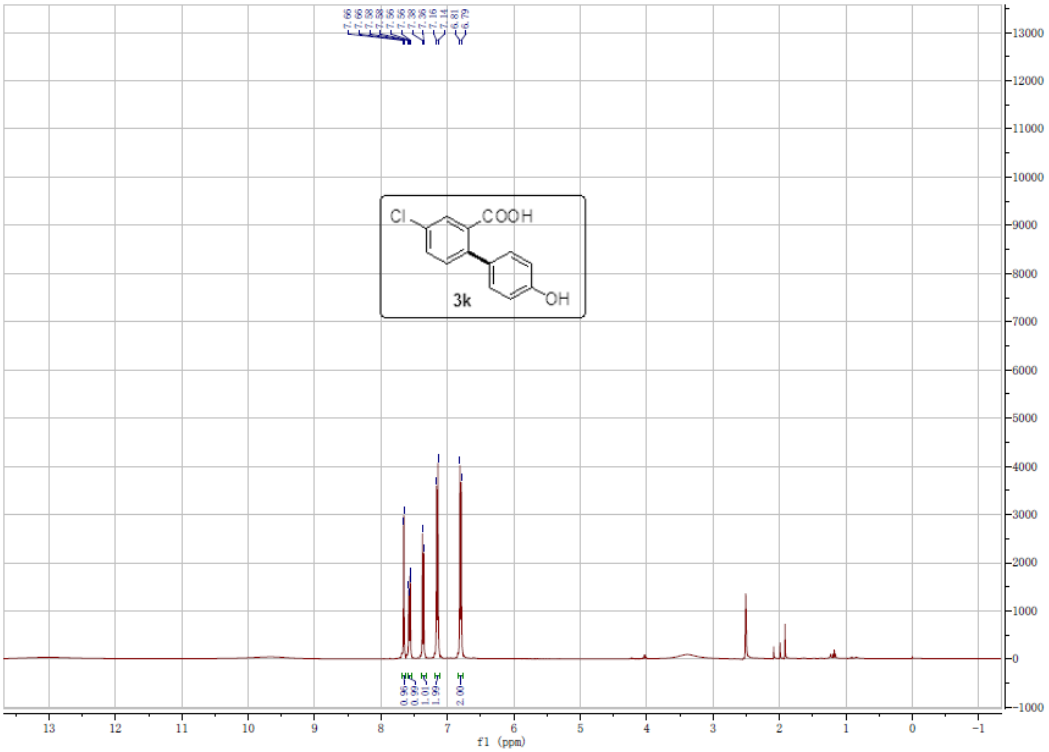


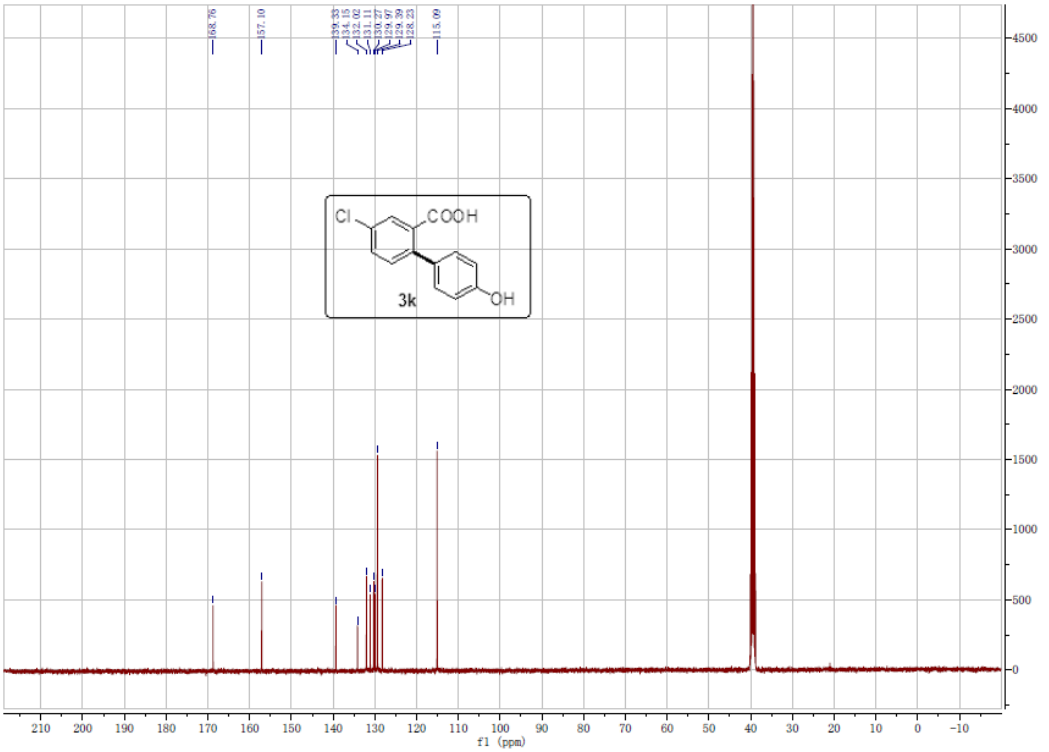
5-Methyl-2-(4-hydroxyphenyl)benzoic acid (3j)



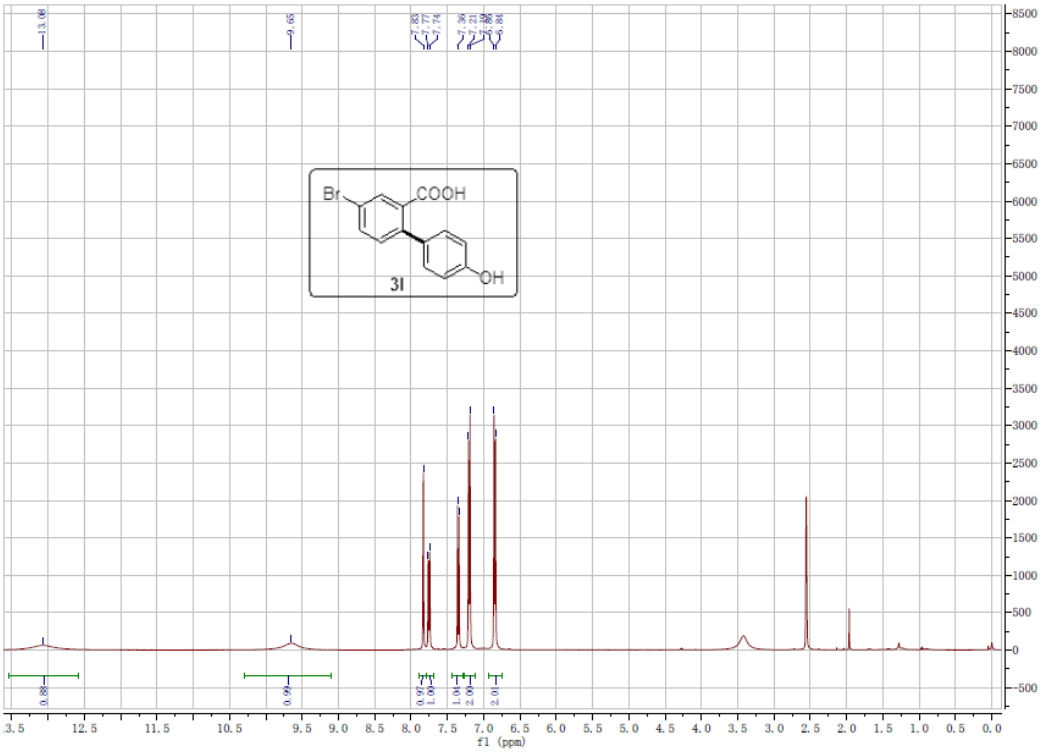


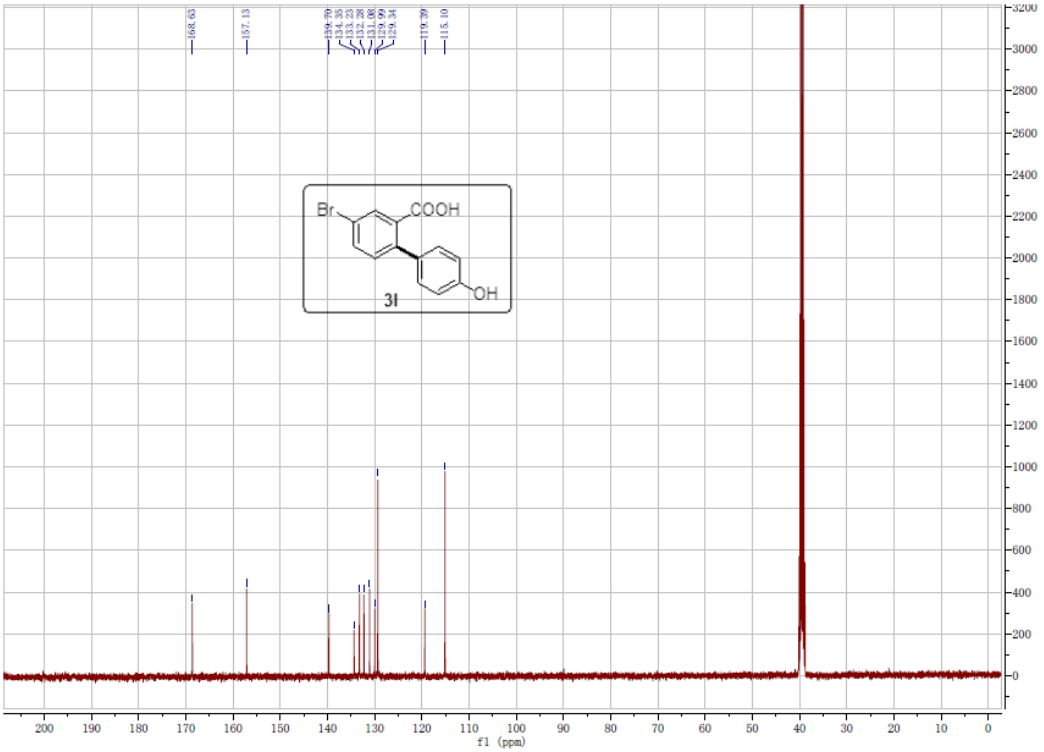
5-Chloro-2-(4-hydroxyphenyl)benzoic acid (3k)



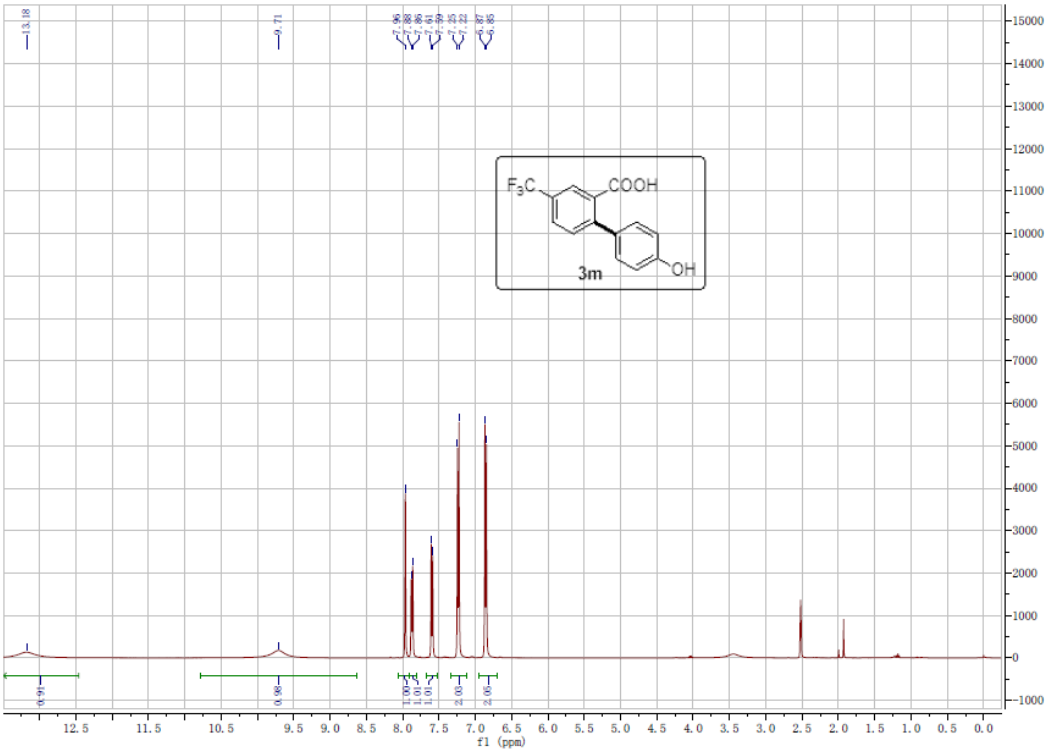


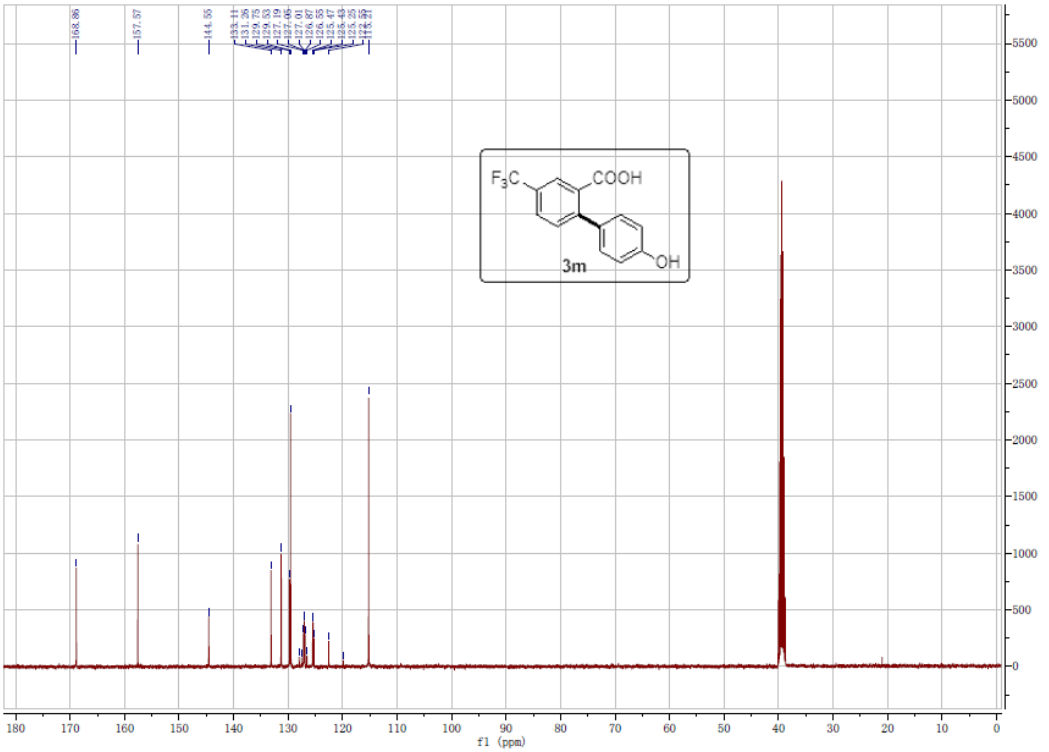
5-Bromo-2-(4-hydroxyphenyl)benzoic acid (3l)



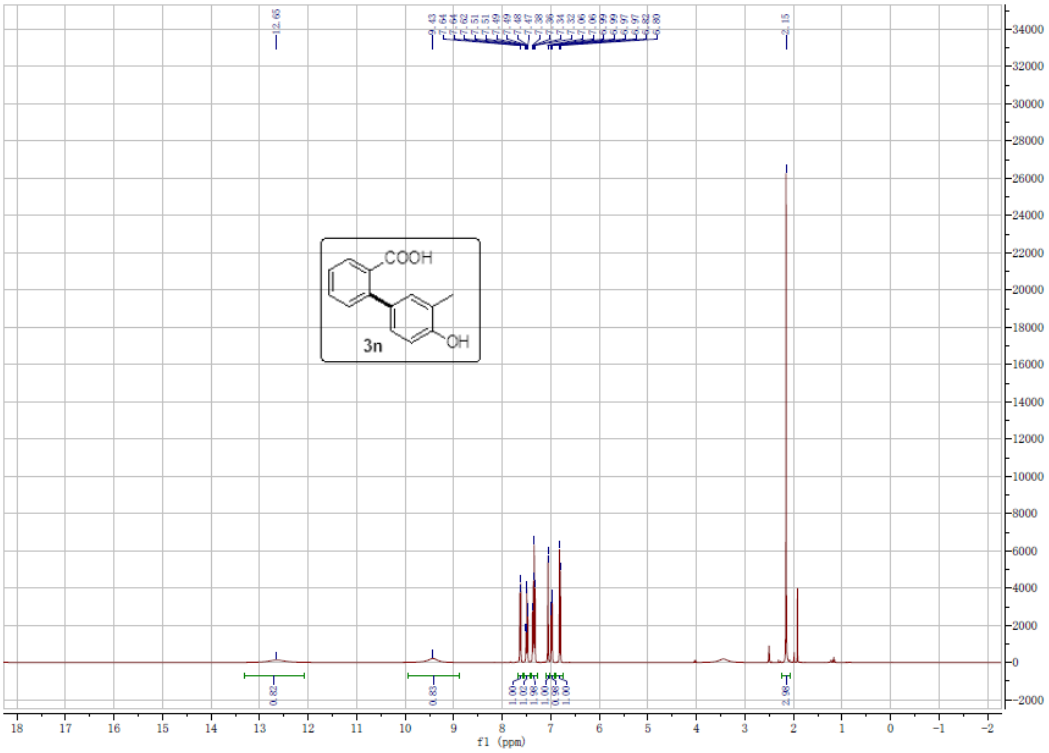


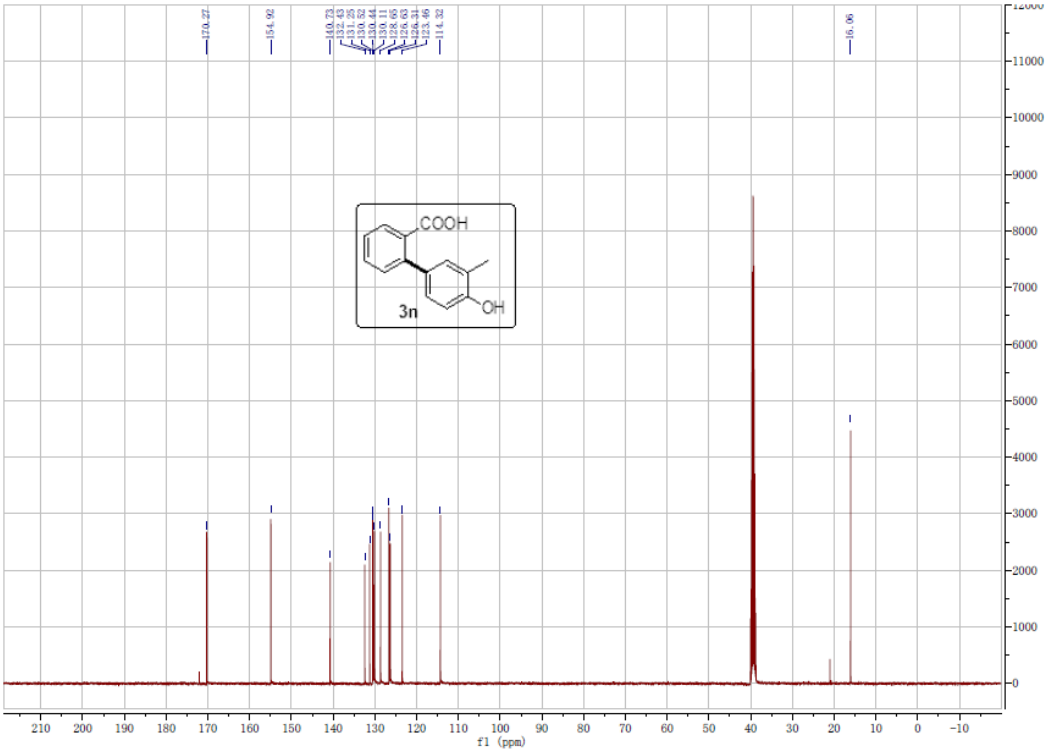
5-Trifluoromethyl-2-(4-hydroxyphenyl)benzoic acid (3m)



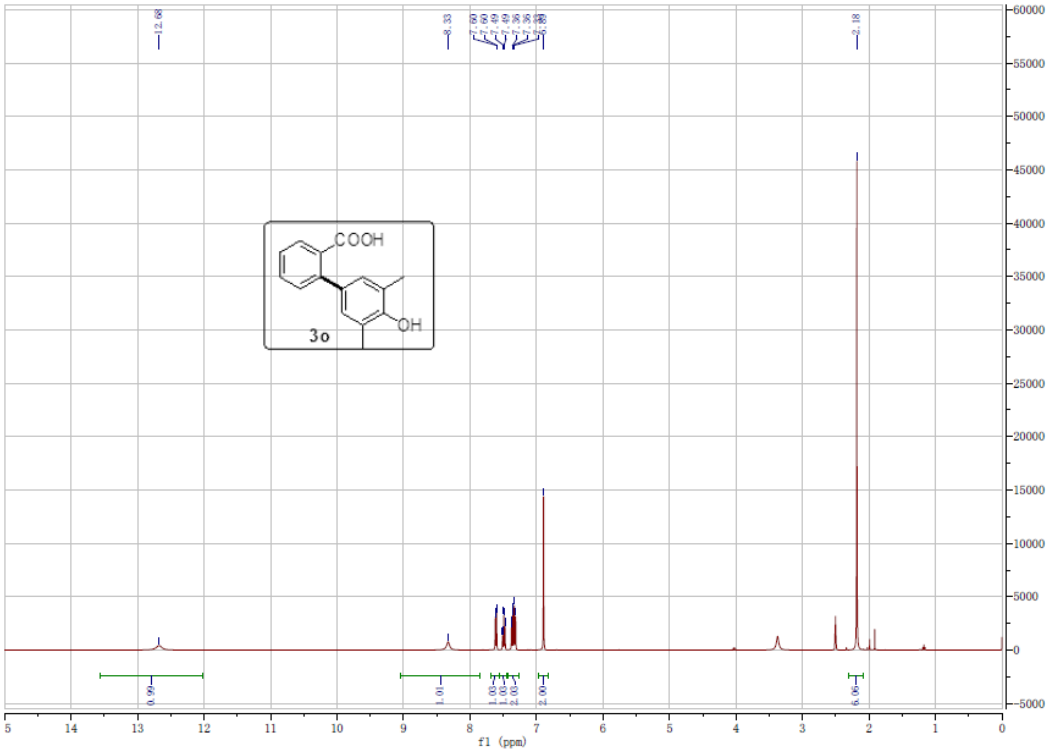


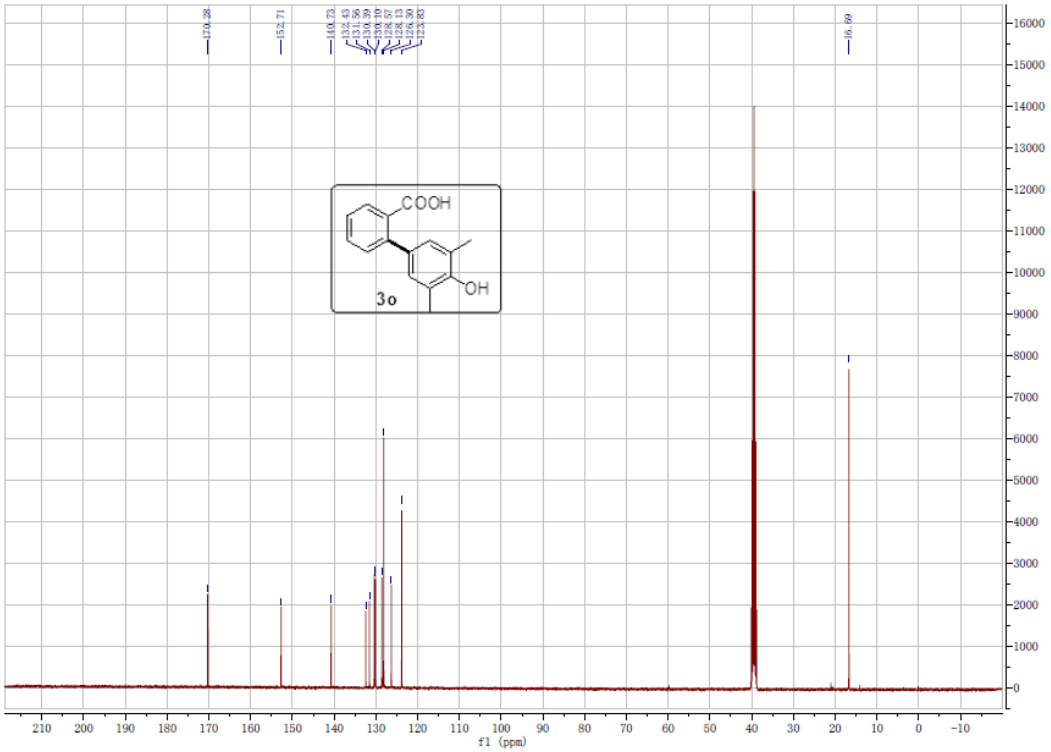
2-(3-Methyl-4-hydroxyphenyl)benzoic acid (3n)



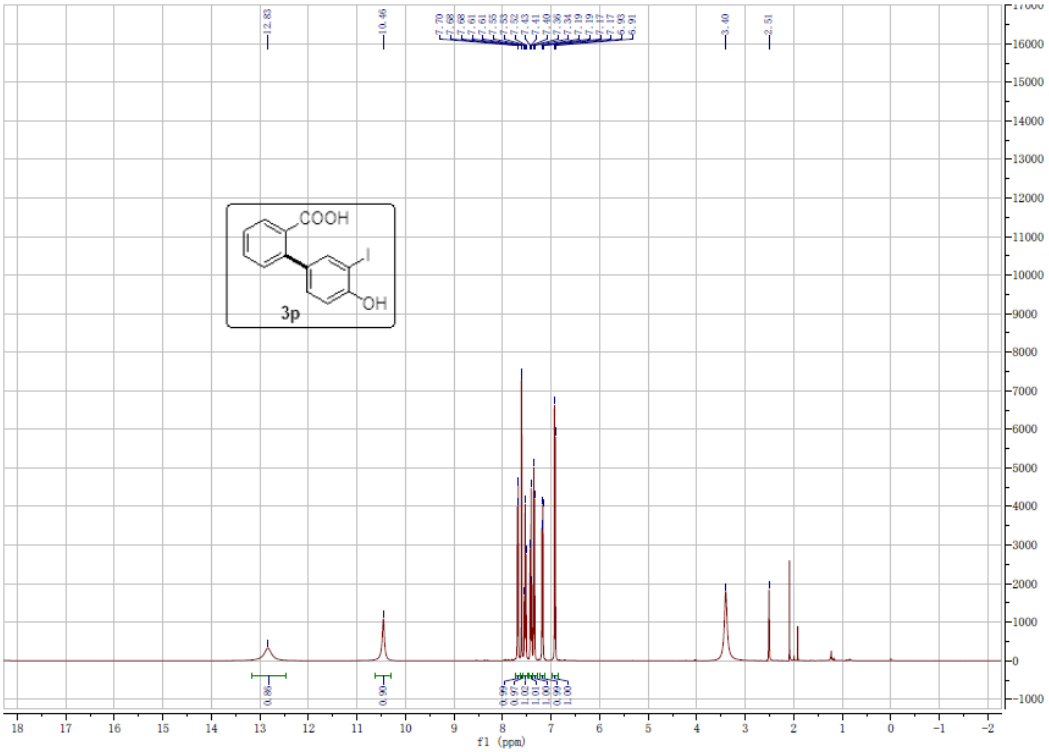


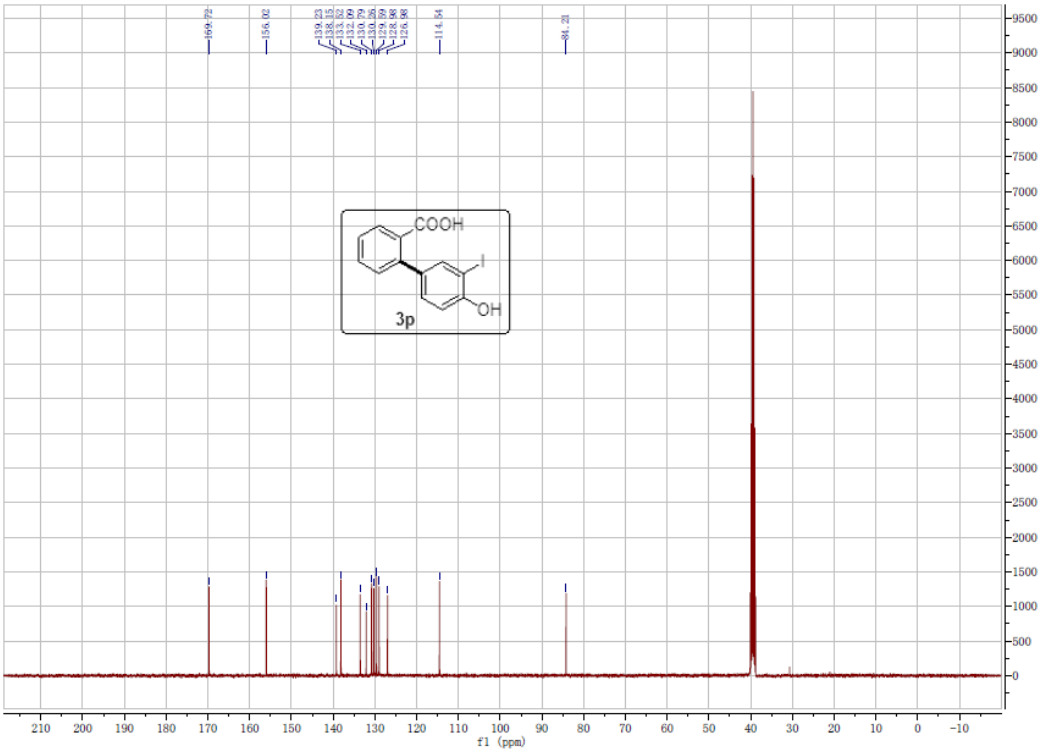
2-(3,5-Dimethyl-4-hydroxyphenyl)benzoic acid (3o)



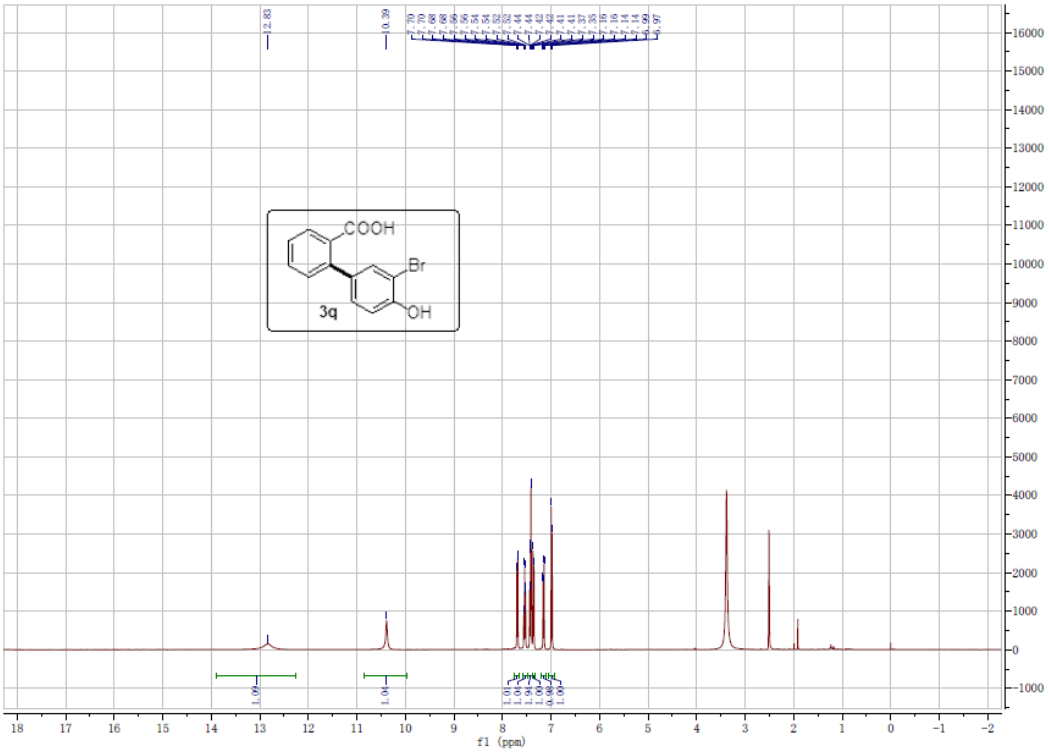


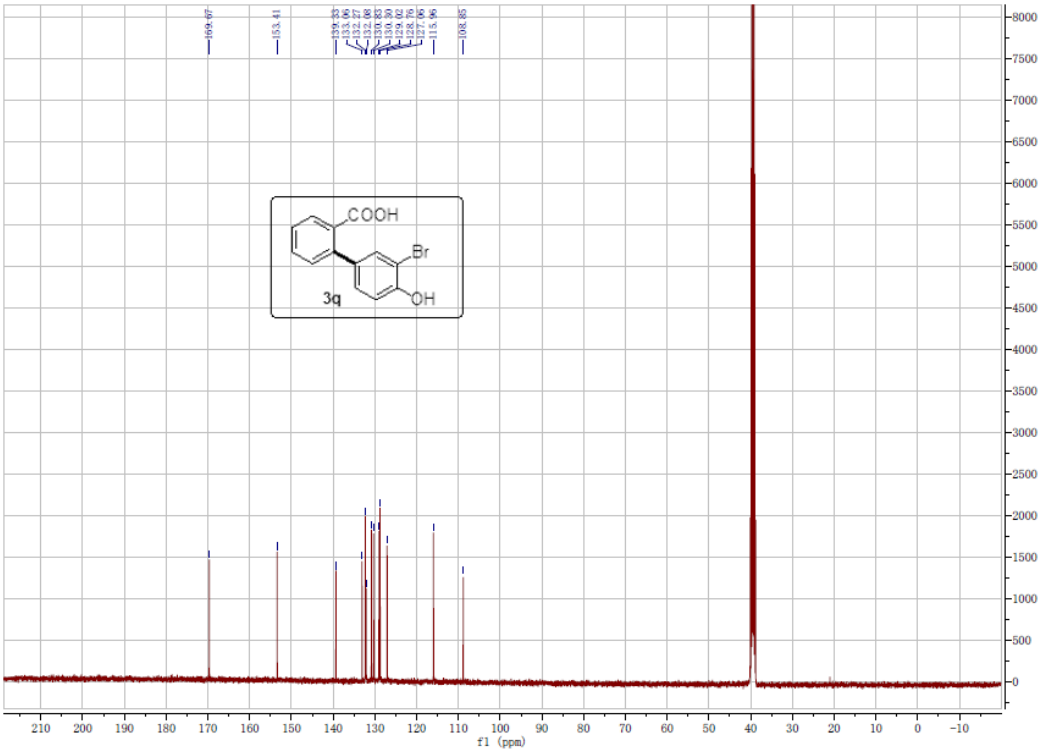
2-(3-Iodo-4-hydroxyphenyl)benzoic acid (3p)



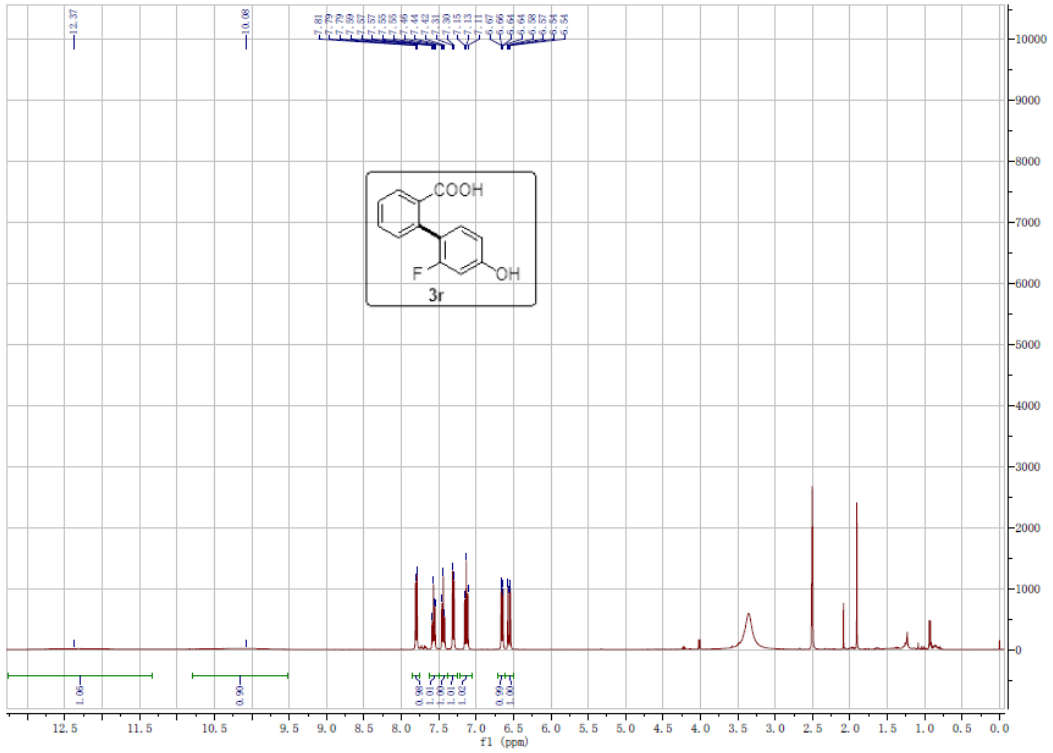


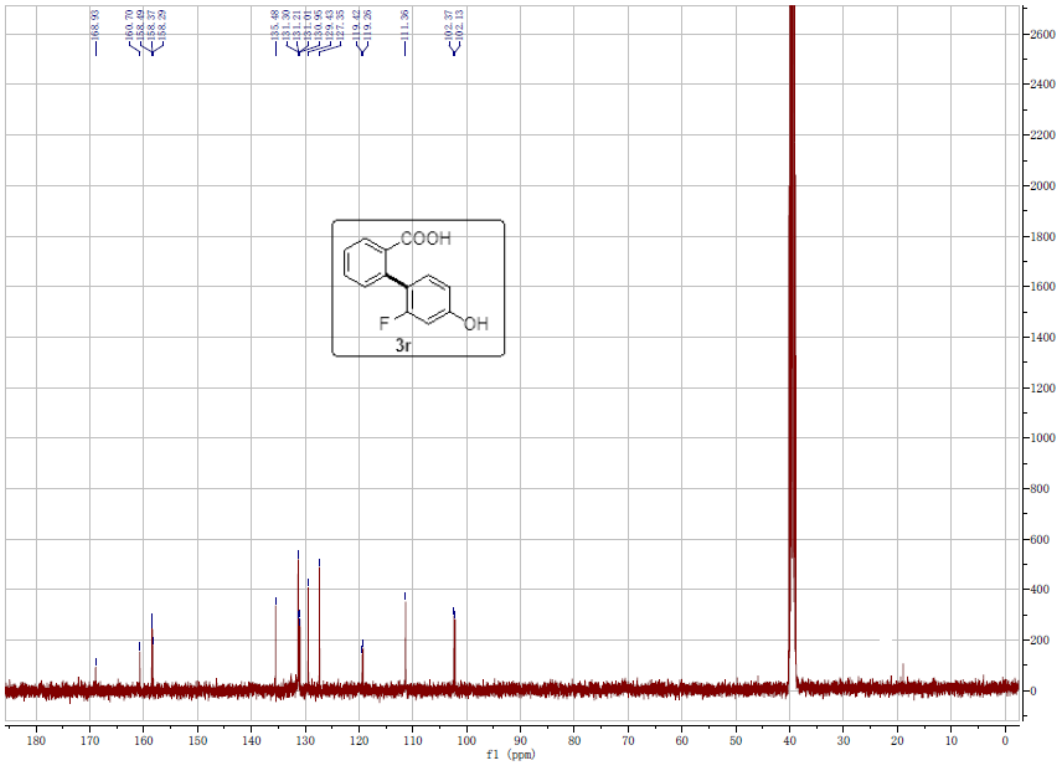
2-(3-Bromo-4-hydroxyphenyl)benzoic acid (3q)



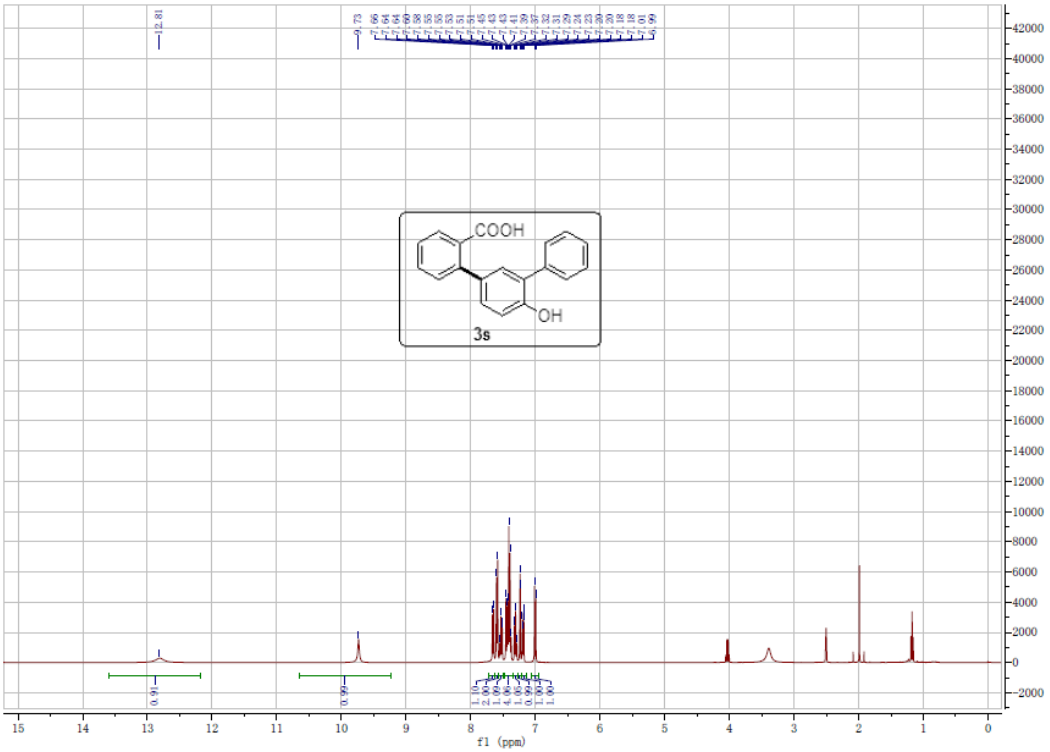


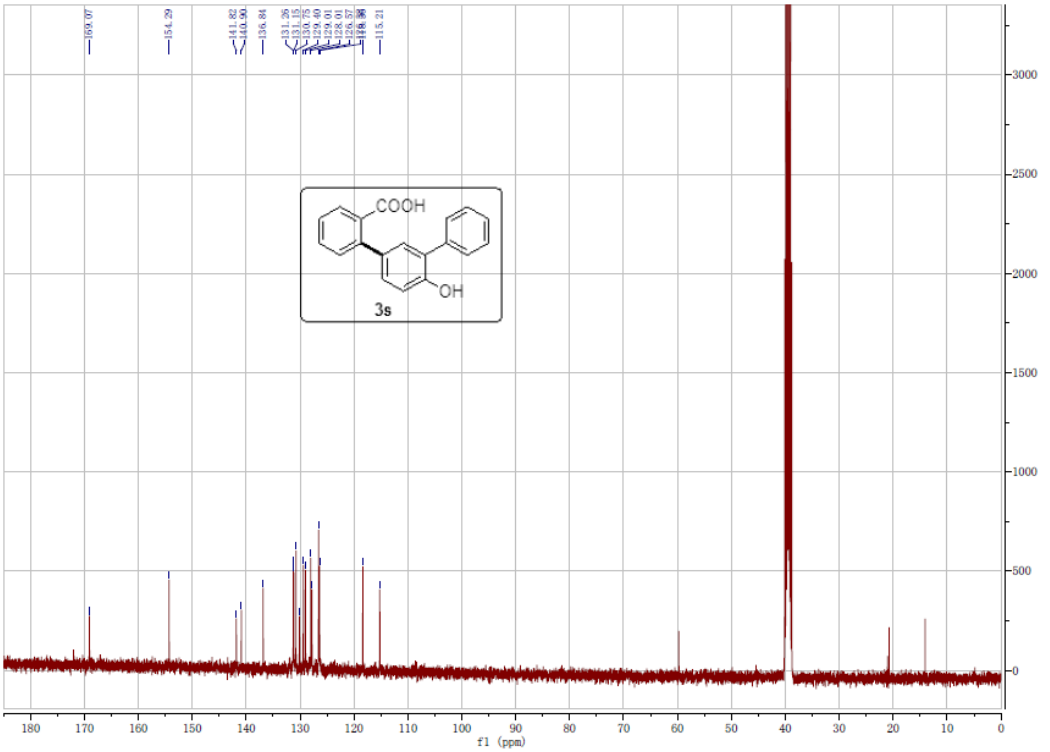
2-(2-Fluoro-4-hydroxyphenyl)benzoic acid (3r)



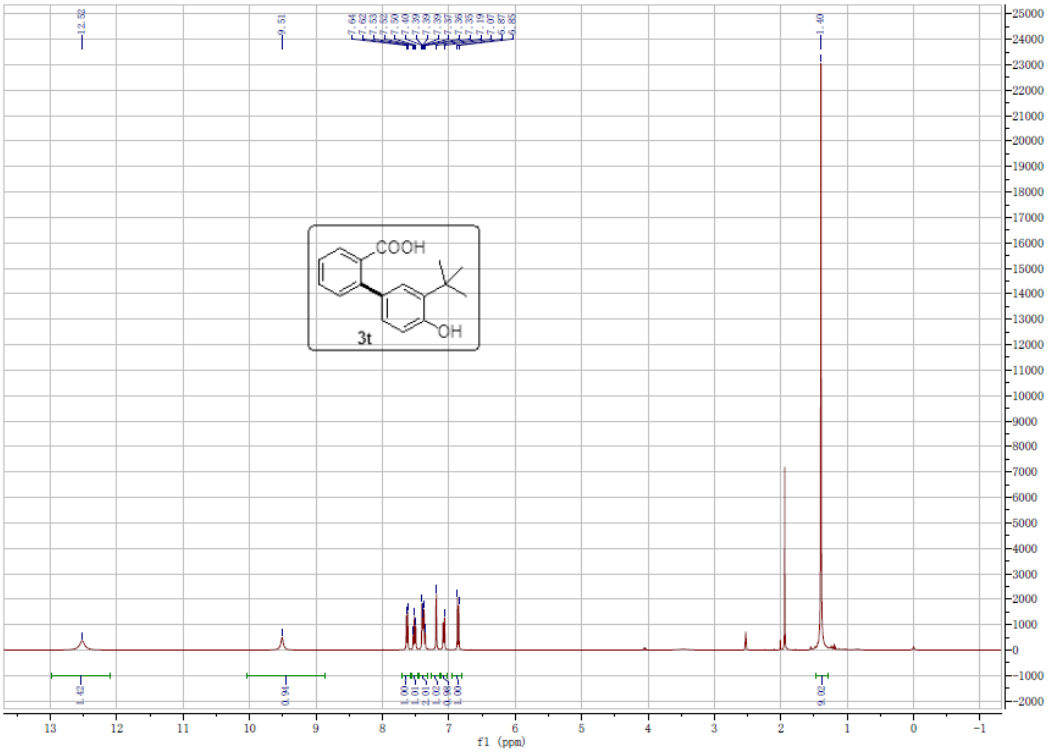


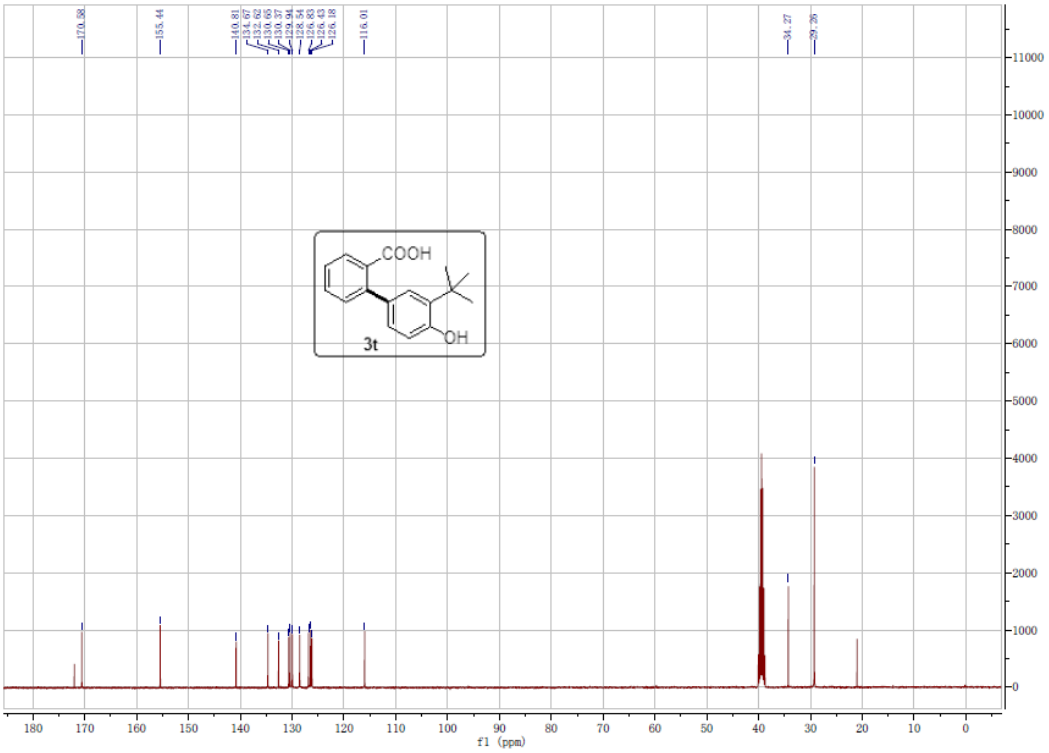
2-(3-Phenyl-4-hydroxyphenyl)benzoic acid (3s)



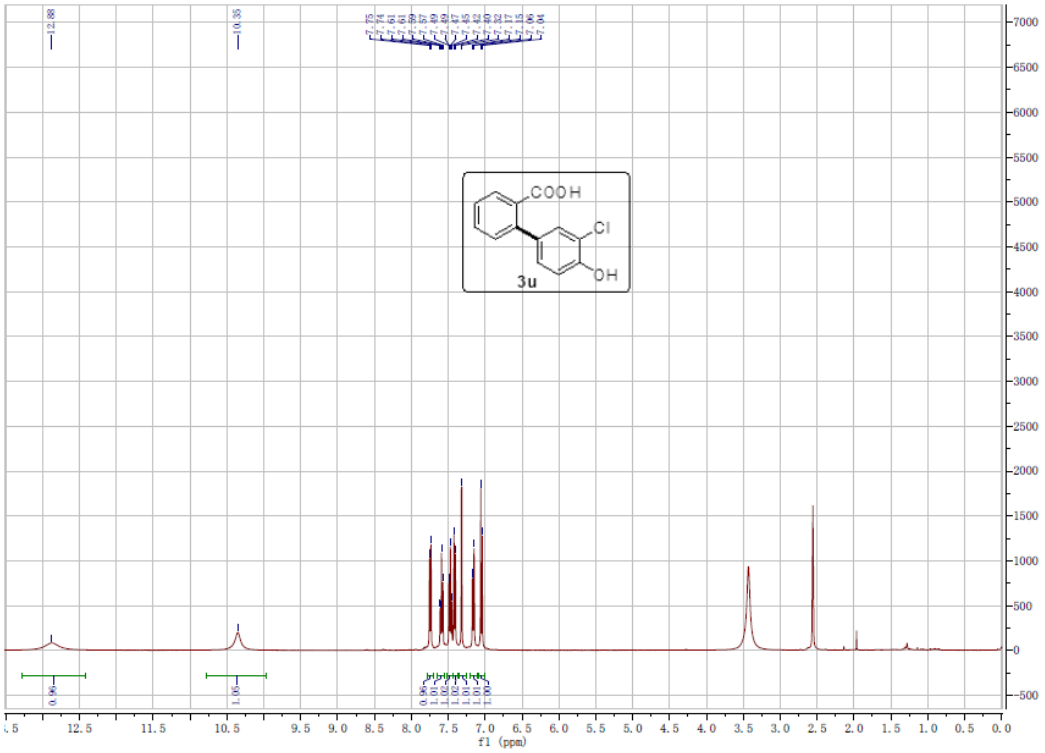


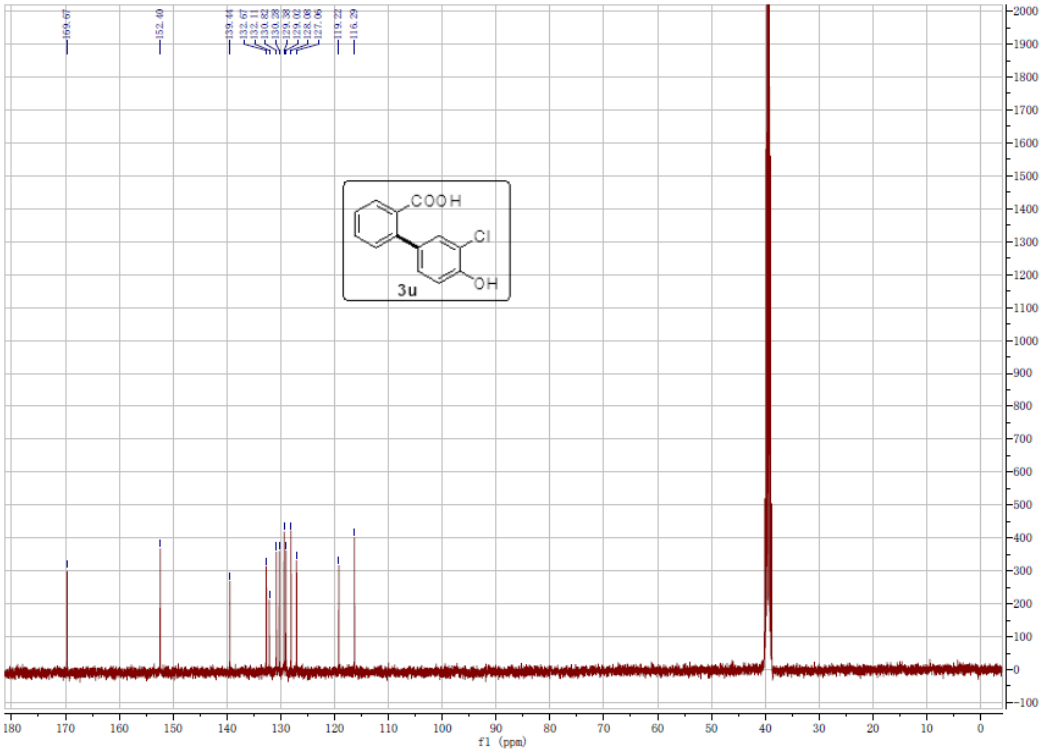
2-(3-*t*-Butyl-4-hydroxyphenyl)benzoic acid (3t)



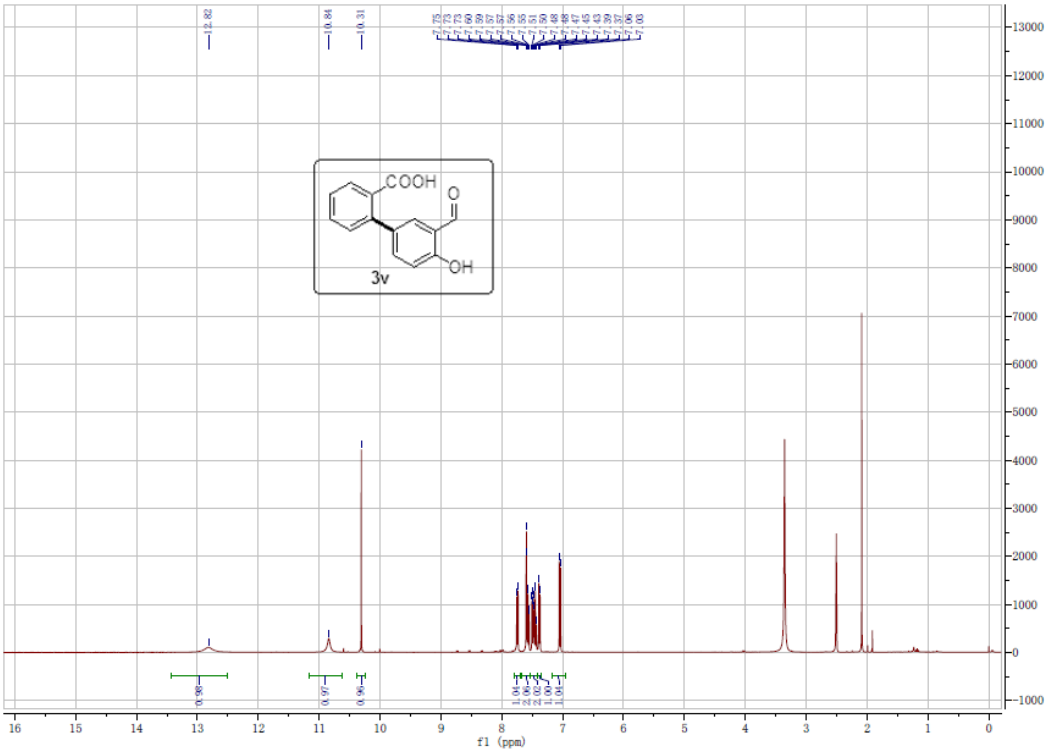


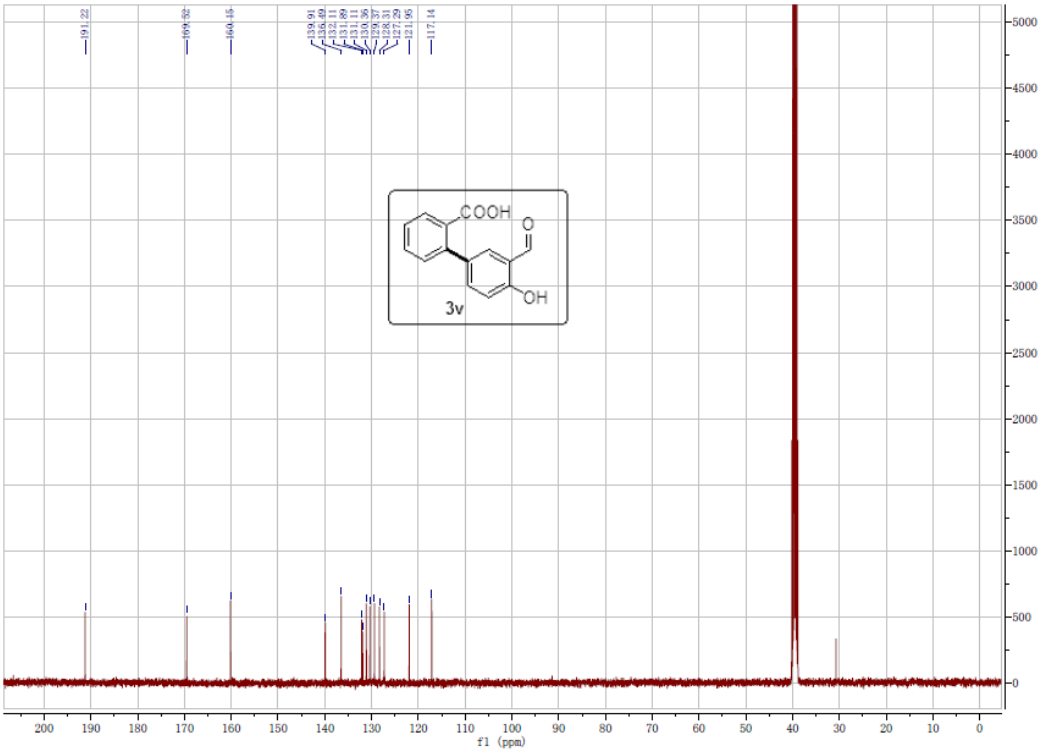
2-(3-Chloro-4-hydroxyphenyl)benzoic acid (3u)



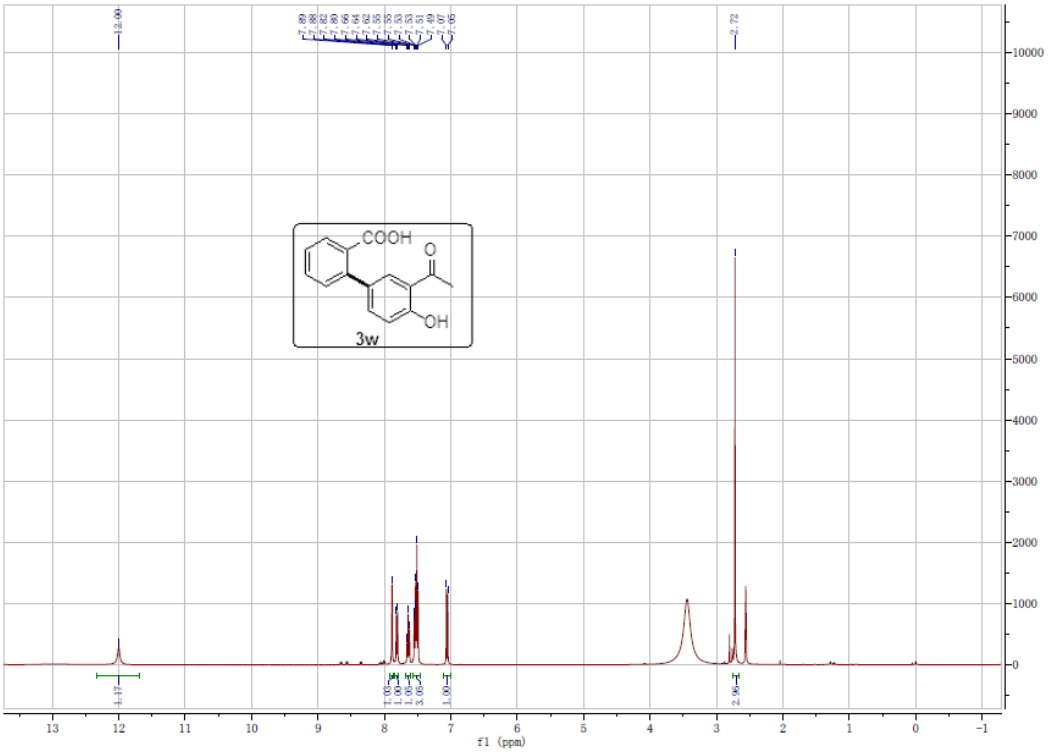


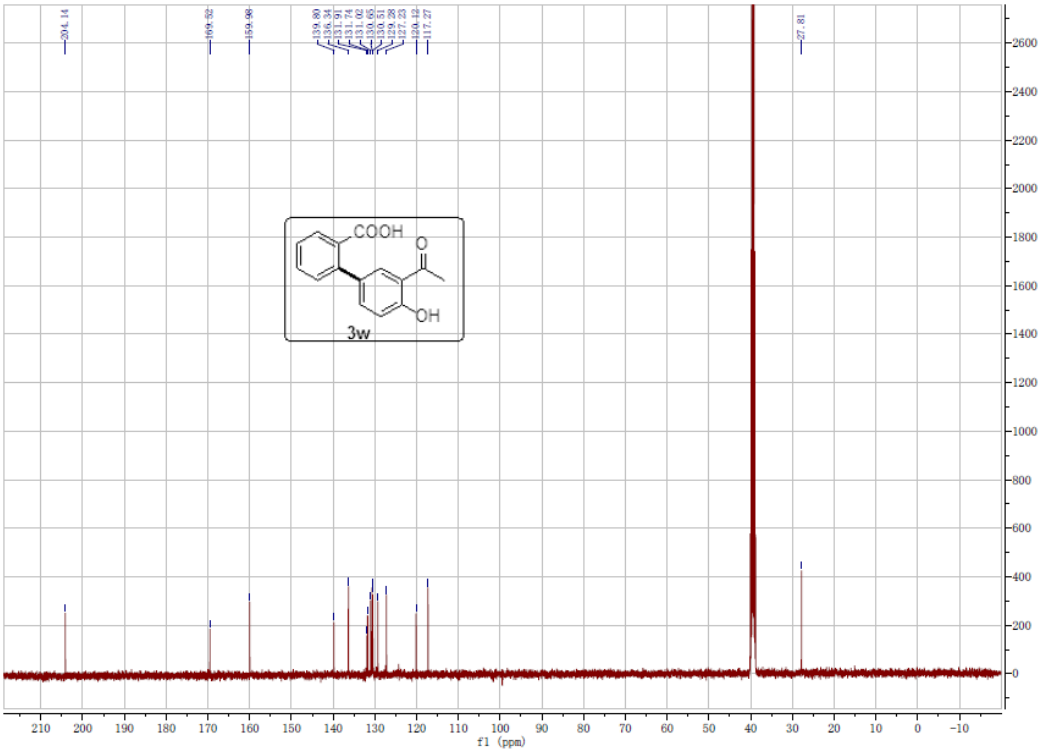
2-(3-Formyl-4-hydroxyphenyl)benzoic acid (3v)



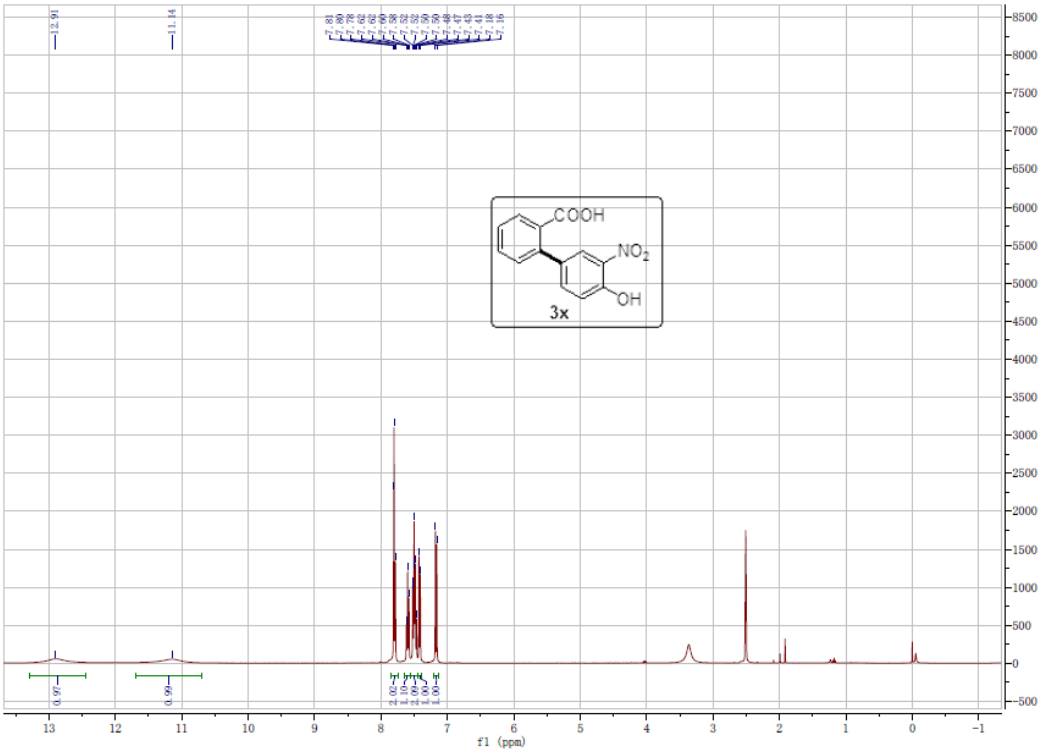


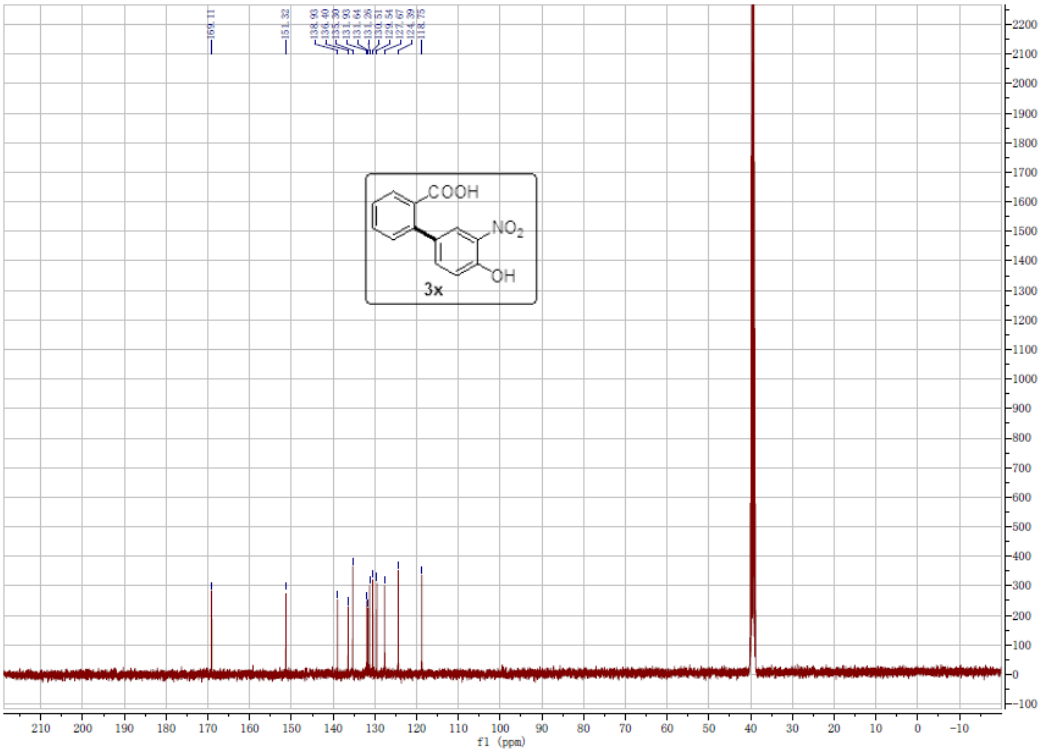
2-(3-Acetyl-4-hydroxyphenyl)benzoic acid (3w)



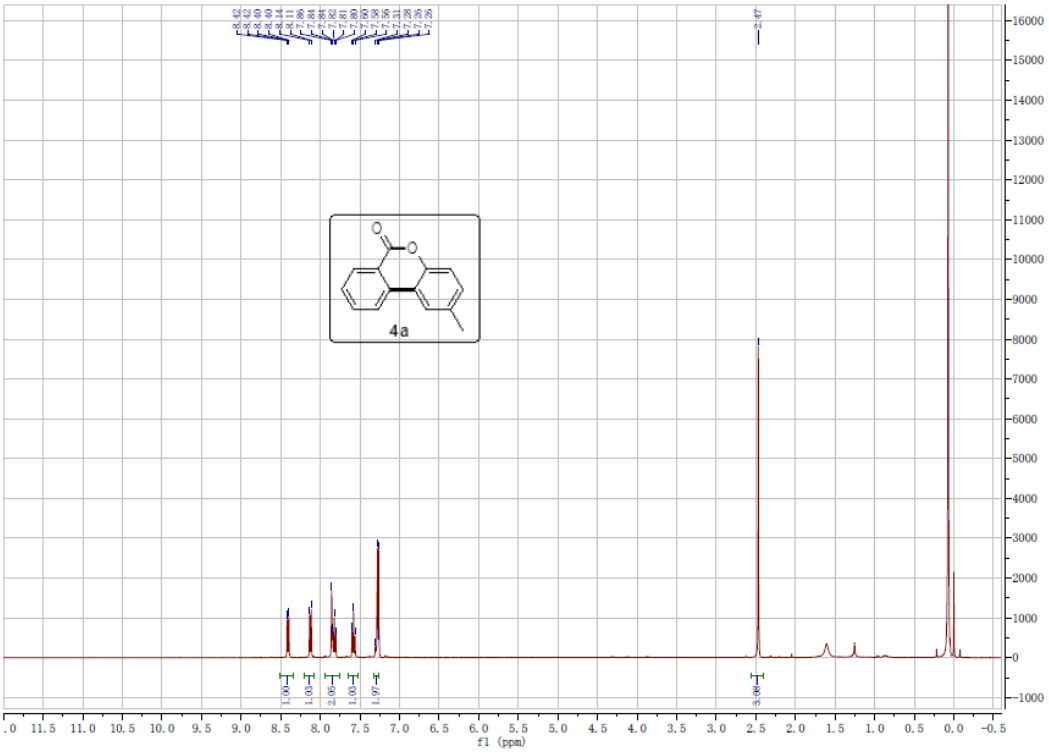


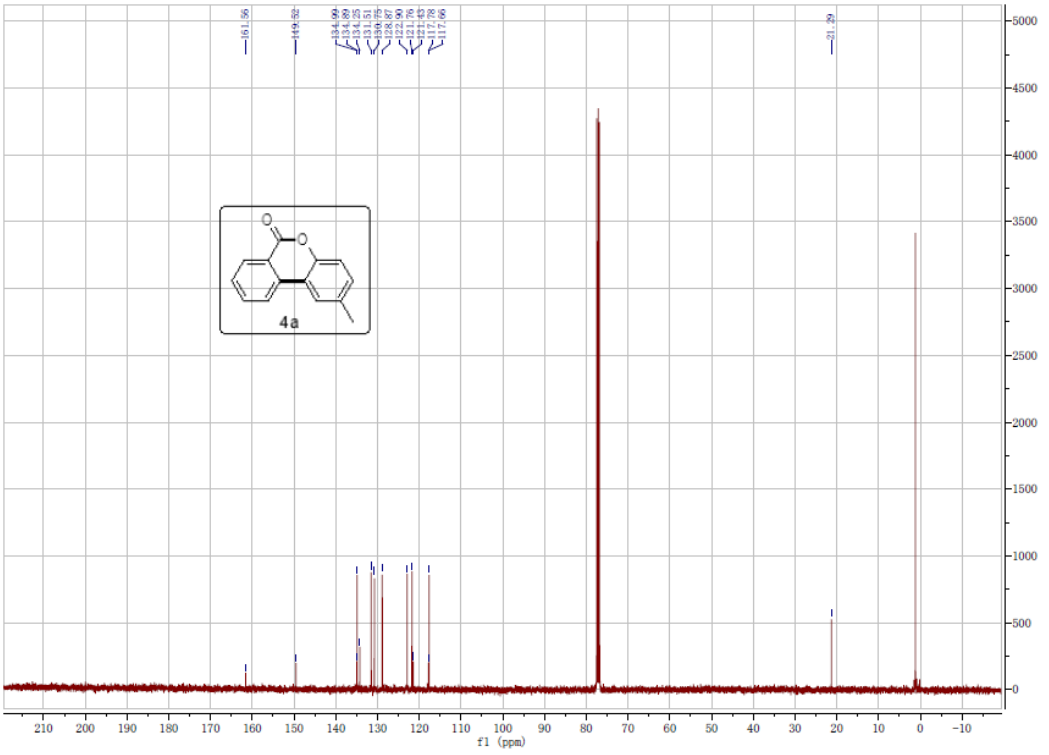
2-(3-Nitro-4-hydroxyphenyl)benzoic acid (3x)



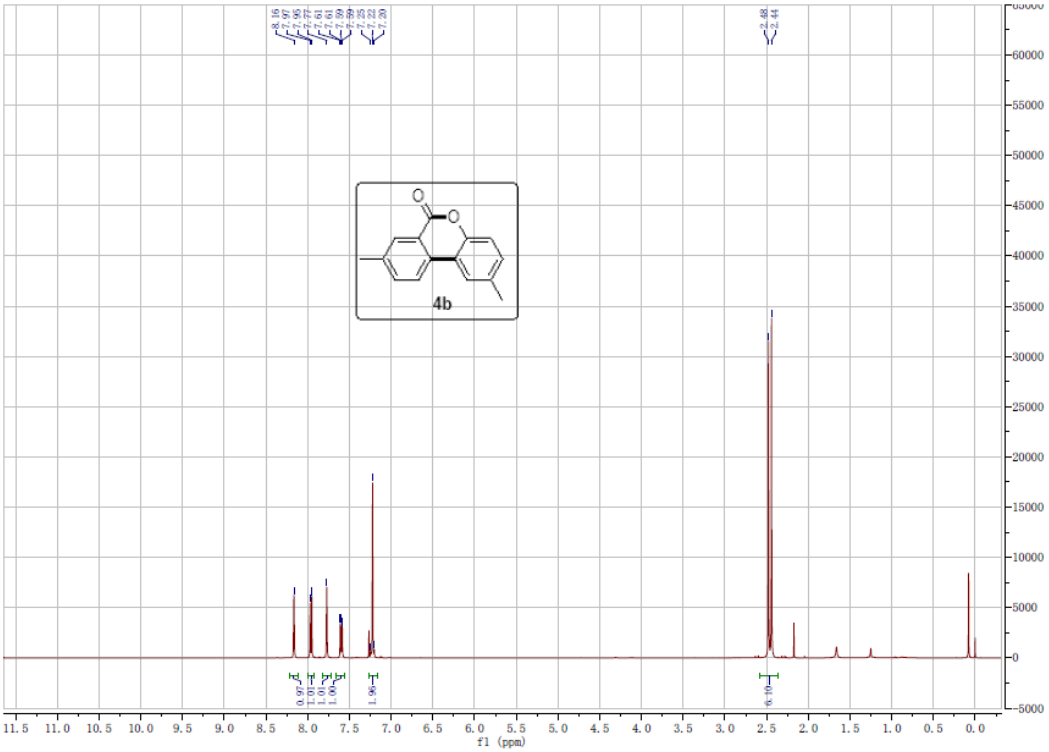


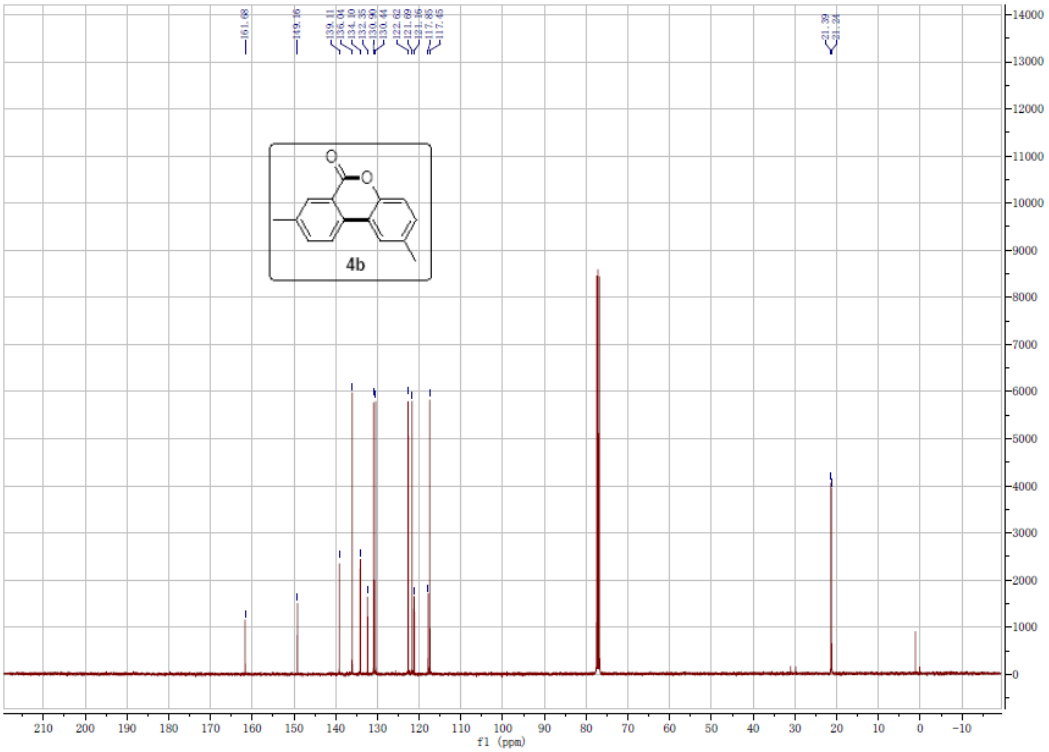
2-Methylbenzo[c]chromen-6-one (4a)



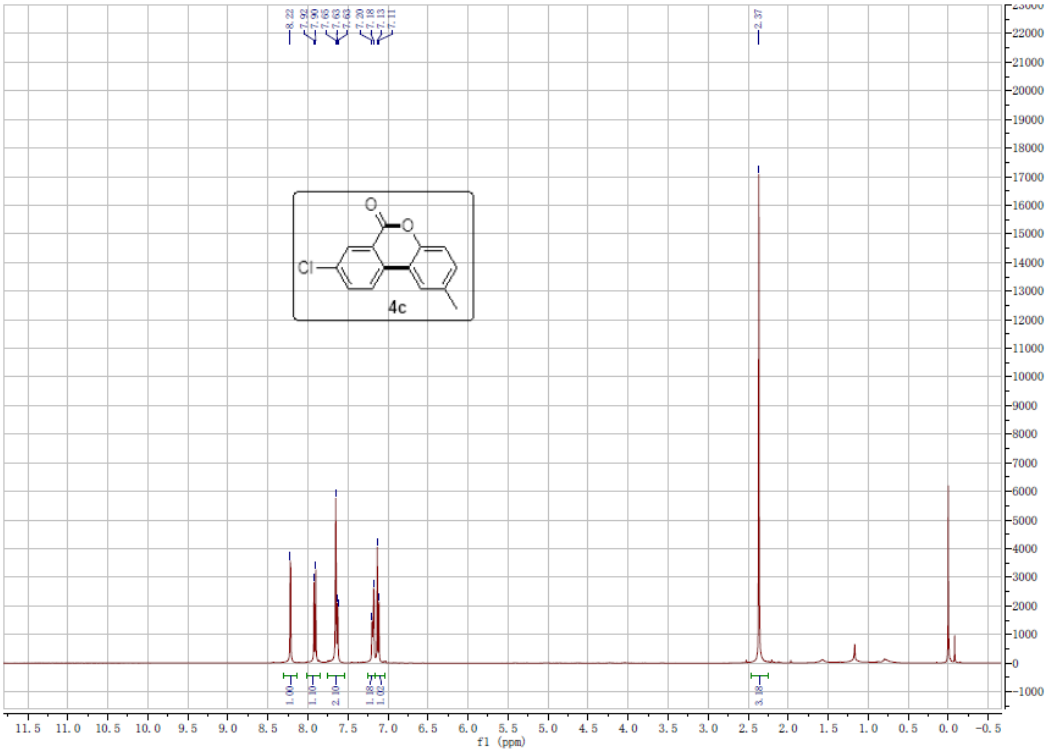


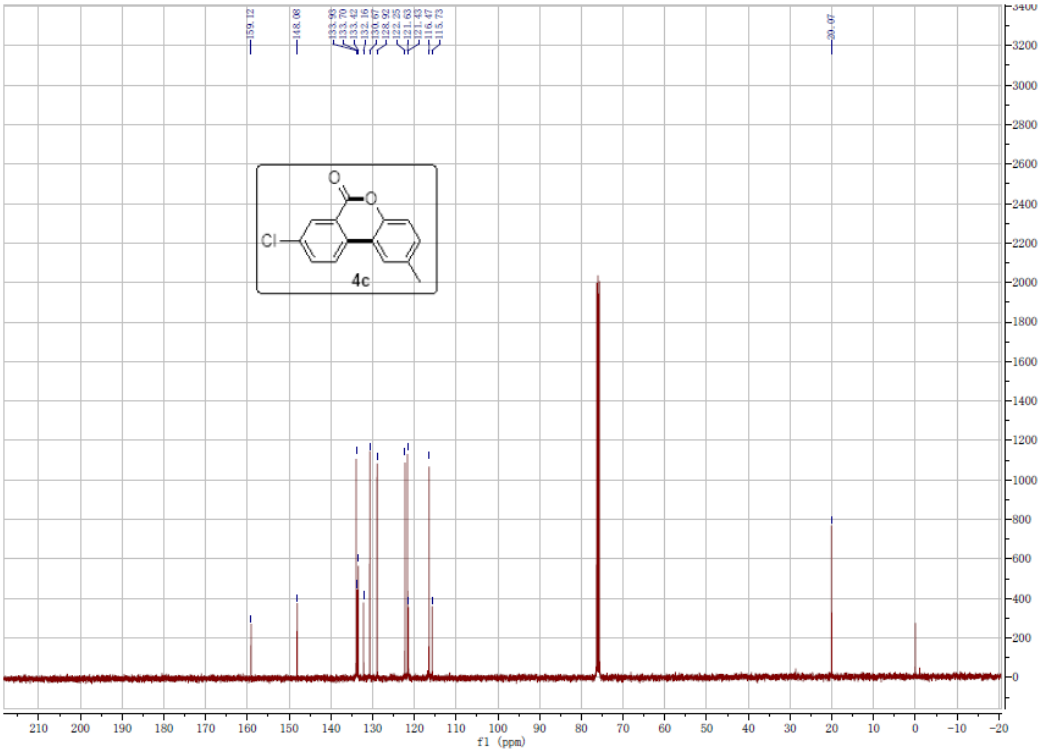
2,8-Dimethylbenzo[c]chromen-6-one (4b)



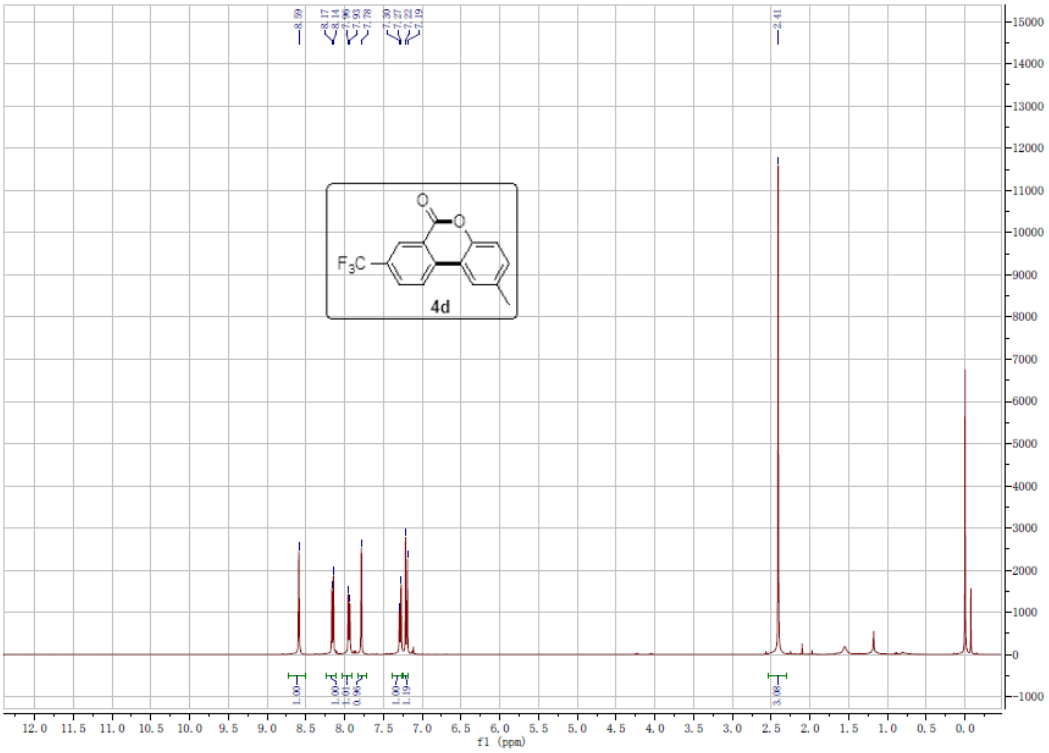


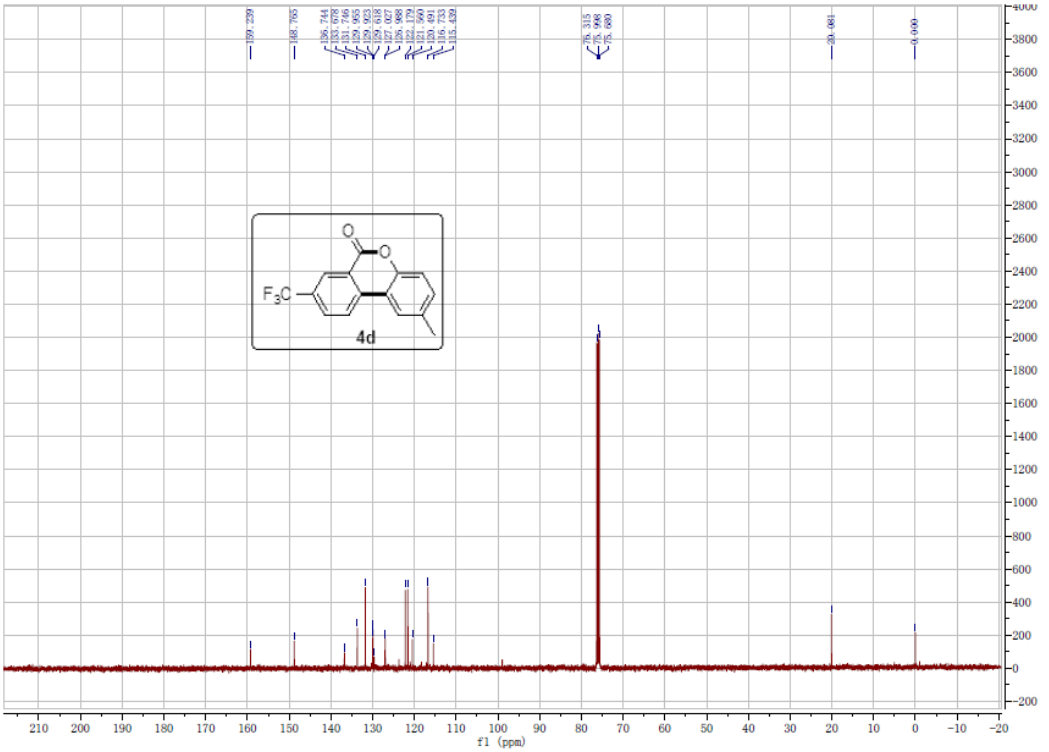
2-Methyl-8-chlorobenzo[c]chromen-6-one (4c)



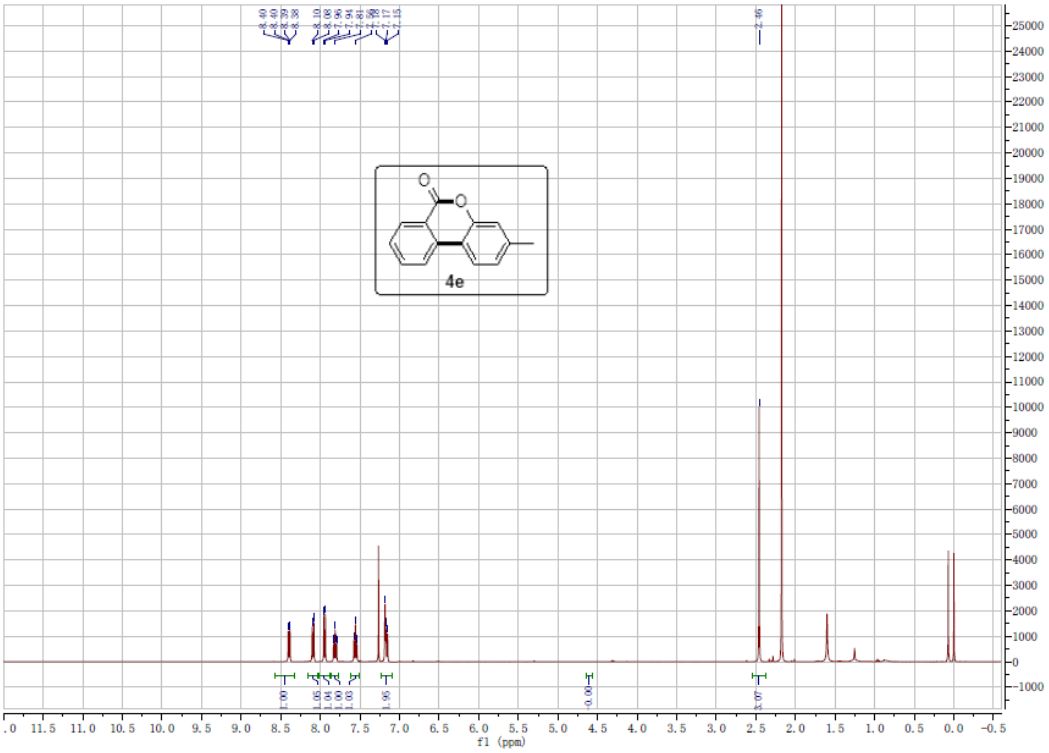


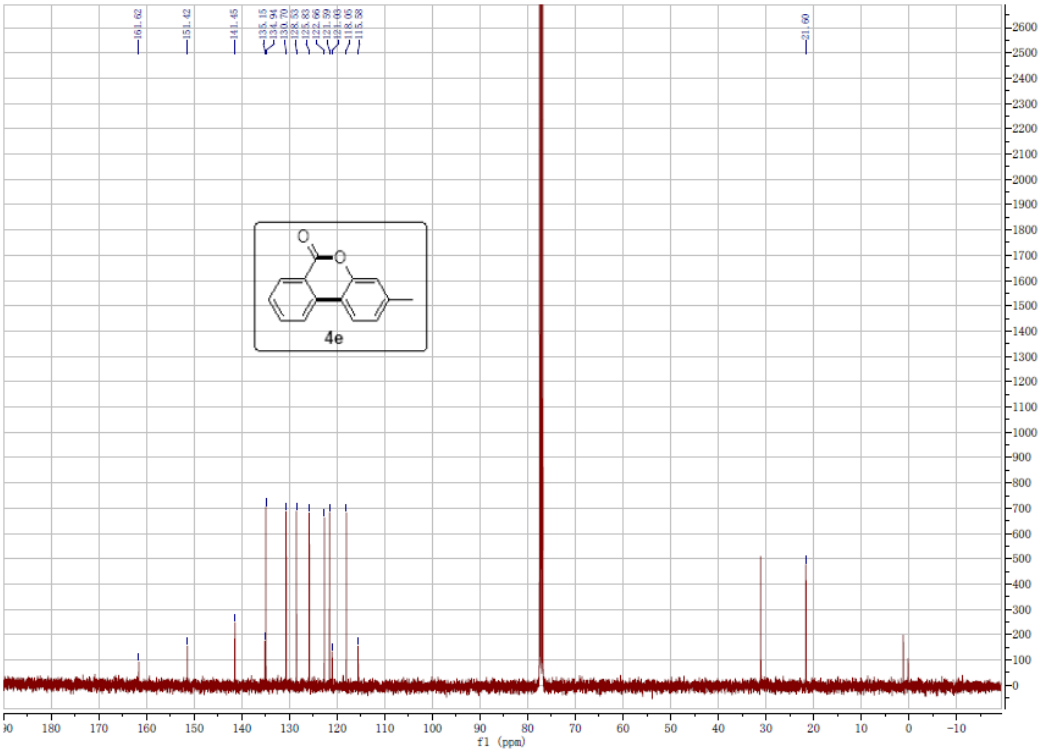
2-Methyl-8-trifluoromethylbenzo[c]chromen-6-one (4d)





3-Methylbenzo[c]chromen-6-one (4e)





7-Methylbenzo[c]chromen-6-one (4f)